Synthesis and rearrangement of silsesquioxane cages

Thesis

Synthesis and Rearrangement of Silsesquioxane Cages

A thesis submitted for the degree of

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獻給我摯愛的父母

To my parents

Statement

The work included in this thesis was carried out by the author during the period November 1997 to October 2001 in the Chemistry Department of the Open University in Milton Keynes under the supervision of Professor Alan Bassindale and Dr Peter Taylor.

Parts of the work have been presented as listed below.

- *21st East-Midlands Regional Meeting, The Royal Society of Chemistry Perkin Division, Lougborough University, UK*, 31st May 2000.
- *Dow Corning Corporation, Midland, USA*, 6th April 2000.
- *The 7th Joint Conference of Chinese Society of Chemical and Technology – UK and the Chinese Section of SCI (Society of Chemical Industry), Brighton*, 18th September 1999.
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Signed

Yuxing Yang

October 2001

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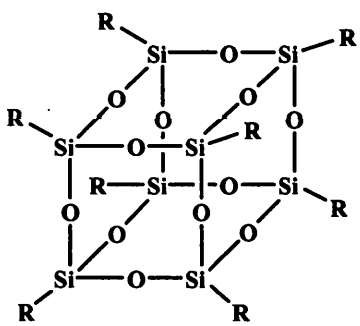
Abstract

The synthesis of octasilsesquioxane cages **(1)** was investigated. A new method was developed which gave a very high yield of octasilsesquioxane cages based on the reaction of alkyltrialkoxysilanes with tetra-*n*-butyl ammonium fluoride solution containing 5% water. In some cases, the reaction gave higher molecular weight cages, such as decasilsesquioxanes **(2)** and dodeca silsesquioxanes **(3)**.



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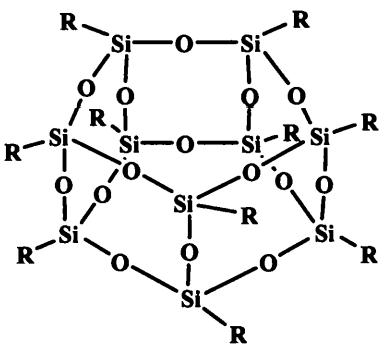

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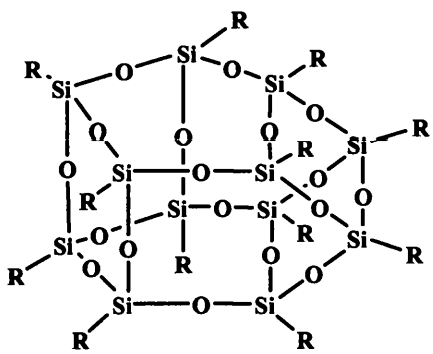
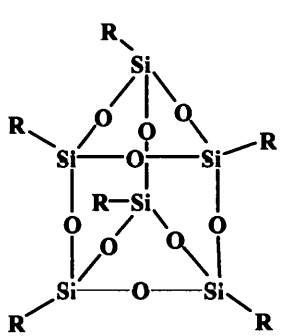


(3)

The rearrangement of octasilsesquioxanes was also investigated. A range of catalysts was employed for these rearrangement reactions, such as sodium acetate, sodium hydroxide, potassium carbonate, sodium trimethylsilanoate and tetra-*n*-butylammonium fluoride solution. Tetra-*n*-butylammonium fluoride solution gave the most remarkable results, in which octasilsesquioxanes cages **(1)** were rearranged to decasilsesquioxane cages **(2)** and dodecasilsesquioxane cages **(3)**.



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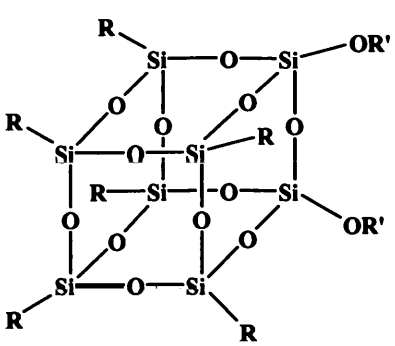
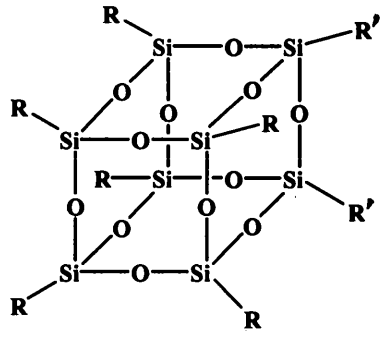


(5)

The hexasilsesquioxane cages **(4)** were synthesised using a number of approaches. The crystal structure of **(4)** was obtained. The rearrangement of **(4)** to give **(1)** was investigated. NMR and HPLC was used to monitor the rearrangement reactions. Partial cages intermediates such as $R_6T_6(OH)_4$, $R_7T_7(OH)_3$ and R_9T_9OH was identified in the reaction mixture.

The rearrangement of **(4)** in the presence of spherosilicate cages gave a novel T_6Q_2 cage **(5)**. Attempts to obtain the X-ray crystal structure of T_6Q_2 failed due to the disordered packing of the groups on the core.

The rearrangement of **(4)** in the presence of alkyltriethoxysilane produced another novel cage, $T_6T'_2$ **(6)**. Again, because of the packing disorder, the X-ray crystallography analysis provided little information of their structure.



(6)

Contents

Abbreviations

AIBN	α, α'-Azoisobutyronitrile
Ar	Aryl group
Br	Broad
Cp	Cyclopentyl
Cy	Cyclohexyl
d	Doublet
DCC	Dicyclohexylcarbodiimide
Dec.	Decomposed
DHB	2,5-Dihydrobenzoic acid
DIC	Diisopropylcarbodiimide
DMF	Dimethylformamide
DMSO	Dmethylsufoxide
EI	Electron Ionisation
ELSD	Evaporative Light Scatter Detector
FT-IR	Fourier Transform Infra red
GC	Gas Chromatography
GPC	Gel Pearmeation Chromatography
HPLC	High Performance Liquid Chromaography
Hz	Hertz
J	Coupling constants
M	Multiplet
MALDI-TOF	Matrix-Assisted Laser Desorption Ionisation Time of Flight
MAS NMR	Magic Angle Spinning Nuclear Magnetic Resonance
NMR	Nuclear magnetic resonance
NOBA	3-nitrobenzyl alcohol

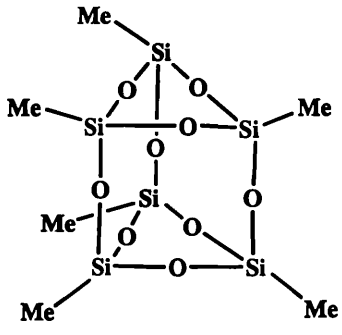
Ppm	Parts Per Million
Psig	Pounds per Square Inch Guage
Q	Quartet
S	Singlet
SEC	Size Excahnge Chromatography
SLPM	Stardard Litre per Minute
T	Triplet
TBAF	Tetra-*n*-butylammonium fluoride
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
TMS	Trimethylsily
TMSCl	Trimethylchlorosilane
Vbr	Very broad

Chapter 1: Introduction

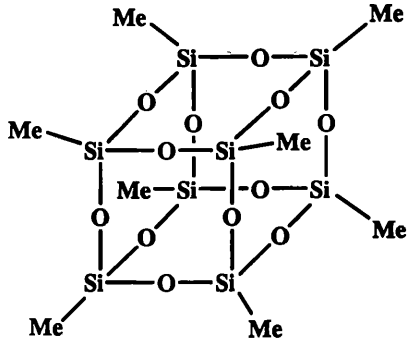
1.0 Introduction

One of the most important types of novel materials based on silicon are the silsesquioxanes, which have the formula, $(RSiO_{3/2})_n$. Although the majority of the research on silsesquioxanes has taken place over the last two decades, the chemistry of such compounds dates back to the second half of the nineteenth century. However, the first silsesquioxane, $(CH_3SiO_{3/2})_n$, was isolated from a mixture of oligomeric silsesquioxanes by Scott in 1946 via the thermal rearrangement of the hydrolysis product of dimethyldichlorosilane and methyltrichlorosilane.[1]

Subsequently, Sprung and Guenther reported[2] the synthesis of hexamethylsilsesquioxane **1.1** and octamethylsilsesquioxane **1.2** from the hydrolysis of methyltriethoxysilane in1955. Octasilsesquioxane cages, $(RSiO_{3/2})_8$, where R = ethyl,[3] *n*-propyl,[4] *n*-butyl,[5] phenyl[6] and cyclohexyl[7] and decasilsesquioxanes, $(PhSiO_{3/2})_{10}$ and dodecasilsesquioxane cages, $(PhSiO_{3/2})_{12}$ have also been synthesised.[6]



(1.1)



(1.2)

However, the first piece of evidence for the cage-like structure of silsesquioxane was not reported until 1960. Larsson and co-workers demonstrated[8] unequivocally the cage structure of the octasilsesquioxane, T_8H_8, by single crystal X-ray crystallography. Twenty years later, the research carried out on silsesquioxanes has dramatically increased because

of their novel physical and chemical properties. Many well-defined polyhedral silsesquioxane frameworks have been prepared, including partial cage frameworks and cages with a wide range of useful functional groups on the core. An increasing number of polyhedral silsesquioxanes have been separated and characterised partly as a result of the improvements in analytical instrumentation. Such results have stimulated an extensive investigation of the chemistry of polyhedral silsesquioxanes.

1.1 Nomenclature of Silsesquioxanes

"Sil", "sesqui" and "oxane" indicates that each silicon atom is connected to one and a half oxygen atoms.[9] The prefix to the name denotes an atom or a group, where the substituents are named on the basis of IUPAC rules. For instance,

$(HSiO_{3/2})_8$ Octahydrosilsesquioxane

$(CH_3SiO_{3/2})_8$ Octamethylsilsesquioxane

Conveniently, a simplified nomenclature of organosilicon compounds exists, which involves the use of the letters M, D, T, and Q, depending upon the number of Si-O linkages, as shown in **Table 1.1**.

From the formula of silsesquioxanes, $(RSiO_{3/2})_n$, the basic silicon unit in the silsesquioxane cage is T. Thus, when n = 6, 8, 10, 12, these polyhedral silsesquioxanes are called hexa, octa, deca and dodecasilsesquioxanes, respectively, i.e. T_6R_6, T_8R_8, $T_{10}R_{10}$, $T_{12}R_{12}$ and T_8H_8 is shown in **Figure 1.1**.

In this thesis, all of silsesquioxanes are simplified using only one substituent to express all the same groups on the core. Such as,

Hexacyclohexylsilsesquioxane: CyT_6

Octacyclohexylsilsesquioxane: CyT_8

Decylphenylsilsesquioxane: PhT_{10}

Dodecylphenylsilsesquioxane: PhT_{12}

For the spherosilicate cages, only express the functional groups, such as,

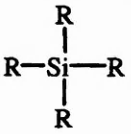
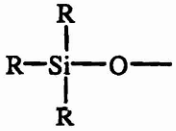
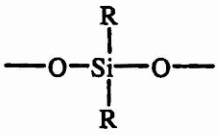
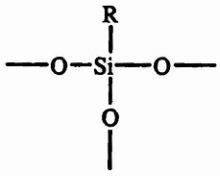
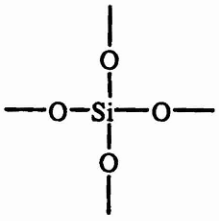
Spherosilicate, $(SiO_{3/2})_6[OSi(CH_3)_3]_6$: Q_6^M

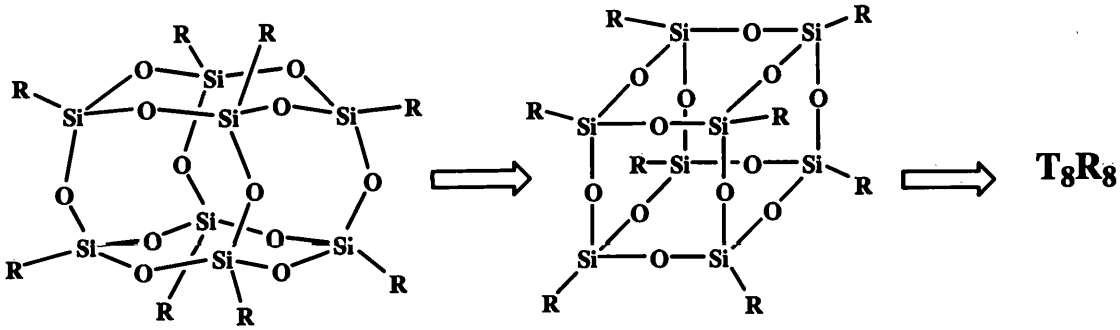
Spherosilicate, $(SiO_{3/2})_8[OSi(CH_3)_3]_8$: Q_8^M

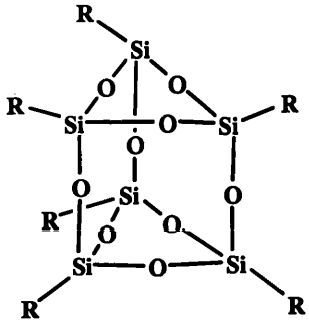
Spherosilicate, $(SiO_{3/2})_8[OSiH(CH_3)_2]_8$: Q_8^H

Spherosilicate, $(SiO_{3/2})_8[OSiH(CH_3)_2CH=CH_2]_8$: Q_8^V

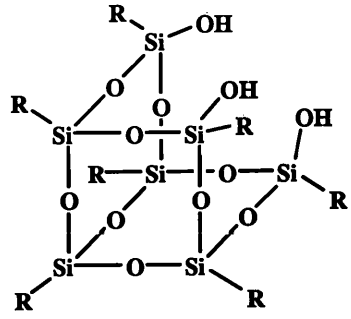
Table 1.1 Nomenclature of Oligosilsesquioxanes

Structure	Composition	Functionality	Symbol
	R_4Si	-	**N**
	$R_3SiO_{1/2}$	Monofunctional	**M**
	$R_2SiO_{2/2}$	Difunctional	**D**
	$RSiO_{3/2}$	Trifunctional	**T**
	$SiO_{4/2}$	Tetrafunctional	**Q**

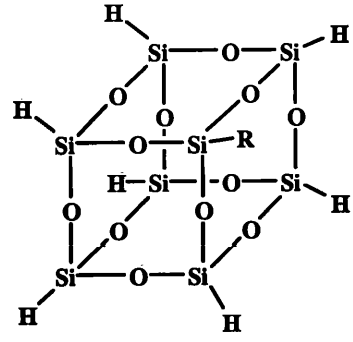




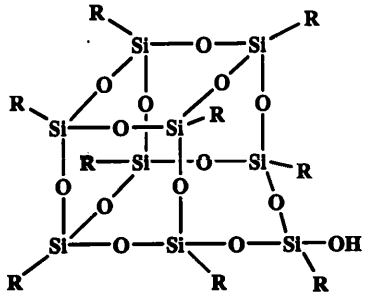
T_6R_6



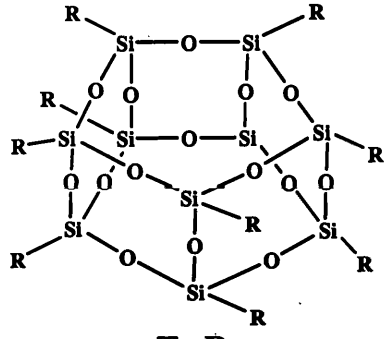
$T_7R_7(OH)_3$



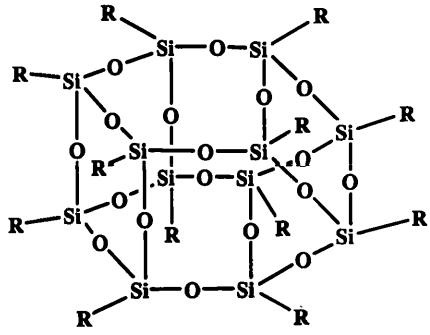
T_8H_8



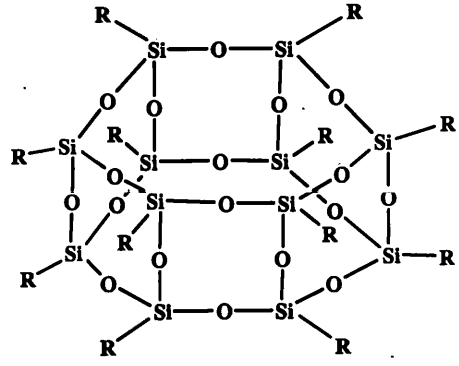
T_9R_9OH



$T_{10}R_{10}$



$T_{12}R_{12}$



$T_{12}R_{12}$

Figure 1.1

1.2 Synthesis of Octasilsesquioxanes

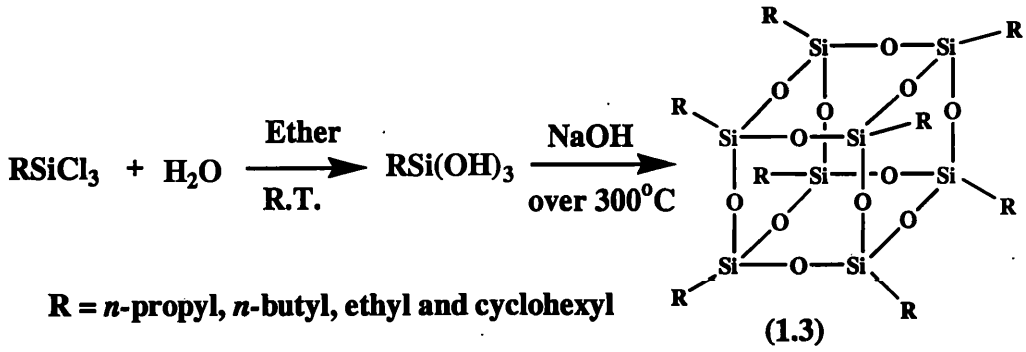
A large number of reactions for the formation of silsesquioxanes cages have been described in the literature. All these reactions can be divided into three major groups, depending on the nature of the starting material. The first category involves the synthesis of silsesquioxanes from organosilicon monomers. Such reactions usually build the polyhedral silsesquioxane framework from trifunctional silane monomers of the type $RSiX_3$, where R is a stable substituent, and X is a highly reactive substituent, such as a chlorine or alkoxy group. The second category involves the synthesis of polyhedral silsesquioxanes from existing Si-O-Si silanol frameworks. The third category uses existing cages and involves reaction of the substituents on the silicon atoms without affecting the skeleton of the polyhedral silsesquioxane.

1.2.1 Synthesis of silsesquioxanes from trifunctional monomers, $RSiX_3$

The most common method used to synthesise octasilsesquioxanes is the hydrolytic condensation of trifunctional monomers. Two kinds of monomers are frequently used, trichlorosilanes and triethoxysilanes, i.e. $RSiCl_3$ and $RSi(OEt)_3$.

1.2.1.1 Hydrolytic condensation of trichlorosilanes, $RSiCl_3$

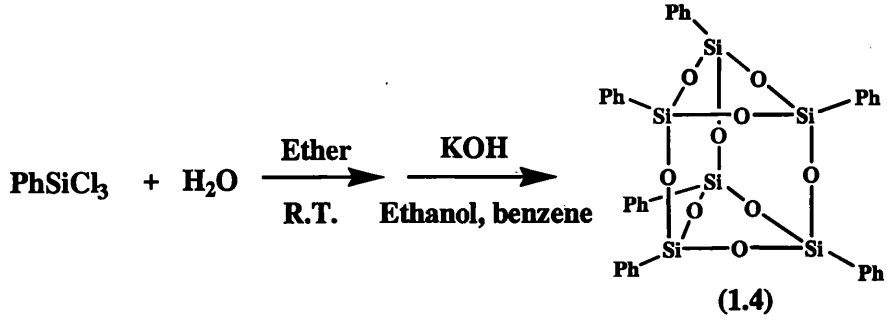
The earliest report of the hydrolytic condensation of trichlorosilane monomers was carried out by Barry and co-workers based on the hydrolysis of $RSiCl_3$ (where R = *n*-propyl, *n*-butyl, ethyl and cyclohexyl) using strong alkalis as catalysts, such as sodium hydroxide and potassium hydroxide.[4] The alkyltrichlorosilane in ether was hydrolysed to the alkyltrisilanol under basic condition, and then condensed to give the pure octasilsesquioxanes **1.3**, as shown in Scheme 1.1. The structures were confirmed by elemental analysis, IR and X-ray diffraction.



Scheme 1.1

They demonstrated that sodium hydroxide or potassium hydroxide catalysed both silanol condensation and siloxane rearrangement at temperatures approaching 300°C. However, under the same conditions, the hydrolysis of 2-methylphenyltrichlorosilane failed to give any octasilsesquioxane. By contrast, the hydrolysis of methyltrichlorosilane produced not only octamethylsilsesquioxane but also dodecamethylsilsesquioxane.

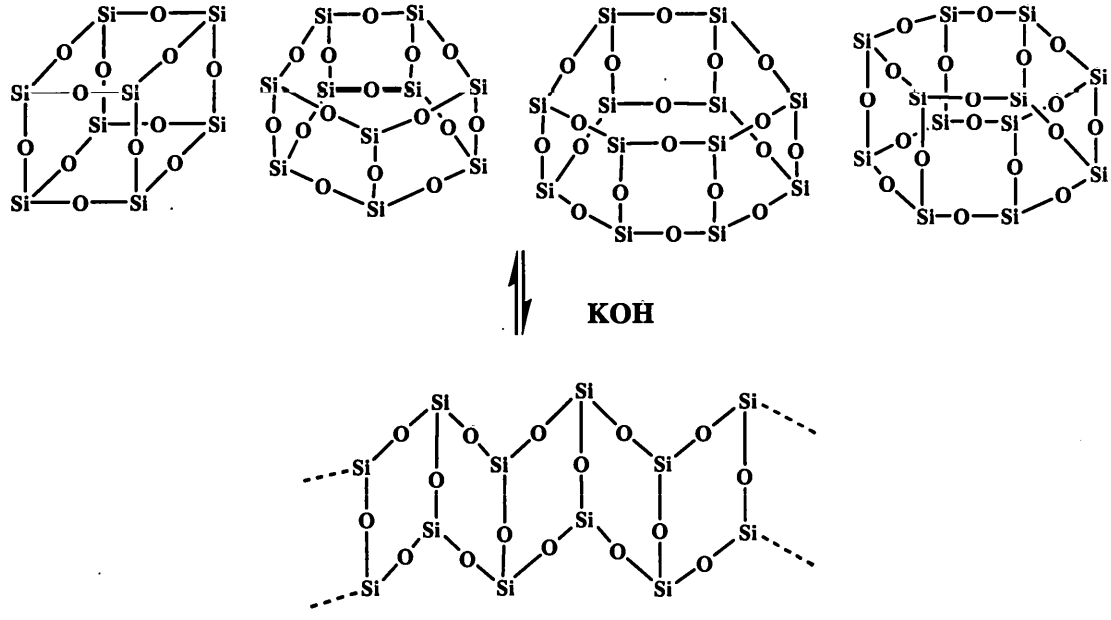
On the other hand, the hydrolysis of phenyltrichlorosilane surprisingly gave a hexaphenylsilsesquioxane **1.4** rather than an octaphenylsilsesquioxane, as shown in Scheme 1.2.



Scheme 1.2

Larsson has subsequently shown[8,10] that the hydrolysis of phenyltrichlorosilane with potassium hydroxide gives the octaphenylsilsesquioxane. In 1964, Brown and co-workers re-investigated this reaction to discover more details of the condensation process.[6] They demonstrated that the hydrolytic condensation of phenyltrichlorsilane could give not only

the octaphenylsilsesquioxane but also the decaphenylsilsesquioxane and dodecaphenylsilsesquioxane. The nature of the solvent played a very important role in determining the type and yield of silsesquioxane formed. The individual silsesquioxane cages were obtained by recrystallisation of the mixture from an alkaline solution of phenyltrichlorosilane in different solvents. Octaphenylsilsesquioxane was precipitated out using benzyltrimethylammonium hydroxide (30% solution in methanol), and was purified by sublimation, because of its poor solubility. However, decaphenylsilsesquioxane was obtained by recrystallisation of the polysilsesquioxanes from a mixed solvent of benzene and hexane. Dodecaphenylsilsesquioxane separated out as large solvated crystals from a solution in acetone, benzene, THF or toluene. Brown also highlighted the complicated kinetic process by which octaphenylsilsesquioxane and dodecaphenylsilsesquioxane were formed by the rearrangement of polysilsesquioxanes in benzene or THF with alkali, alcohol and water.

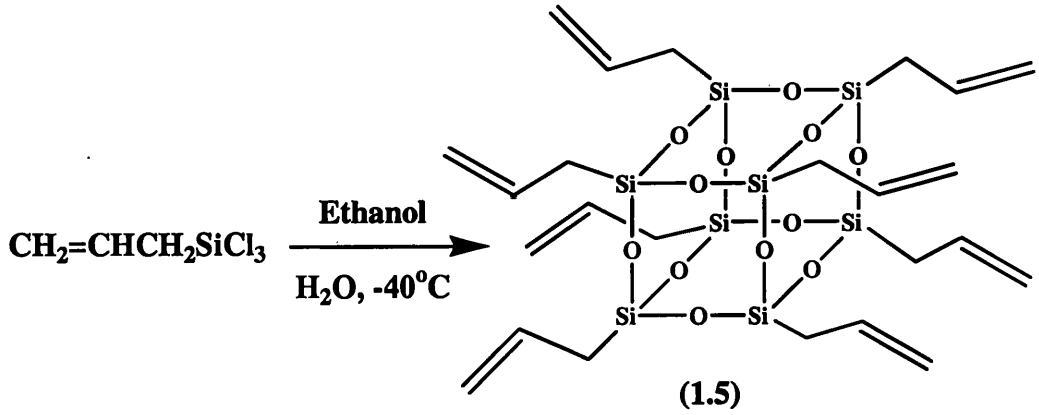


***Cis*-syndiotatic double chain**

Scheme 1.3

They suggested that an intermediate was produced prior to octaphenylsilsesquioxane condensation, and this intermediate was assumed to be a ladder-like silsesquioxane, such as a *cis*-syndiotactic double chain. This *cis*-syndiotatic double chain is in equilibrium with a range of phenylsilsesquioxanes, as shown in Scheme 1.3.

In 1983, Martynova and co-workers described[11] the preparation of octaallylsilsesquioxane obtained by the hydrolysis of allyltrichlorosilane in ethanol at -40°C. The allyltrichlorsilane was added drop-wise to ethanol, followed by water. The mixture was kept cool for 20 hours, then methanol added, or bubbling liquid nitrogen vapour passed through the solution, leading to the precipitation of octaallylsilsesquioxane **1.5** from the mixture in high yield (13%), Scheme 1.4. octaallylsilsesquioxane **1.5** was purified by sublimation and the structure of **1.5** was confirmed by single crystal X-ray crystallography.

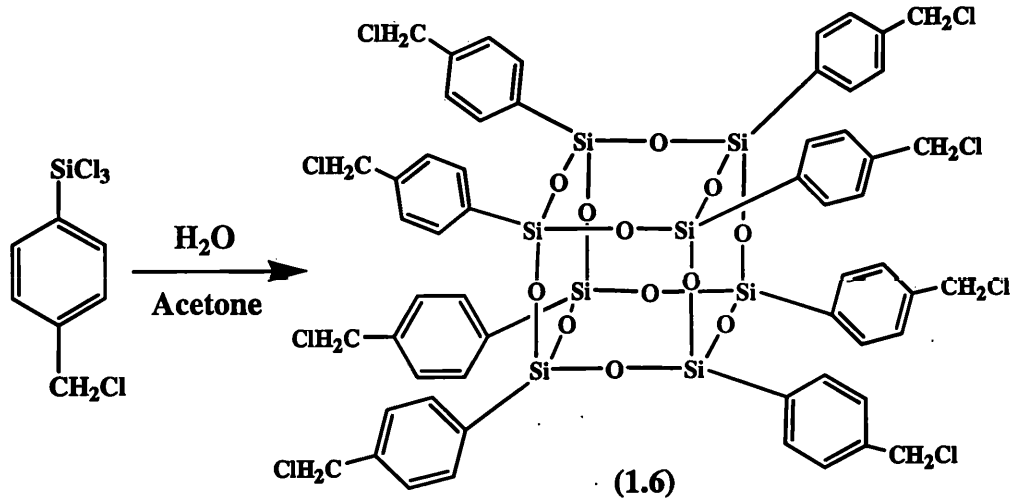


(1.5)

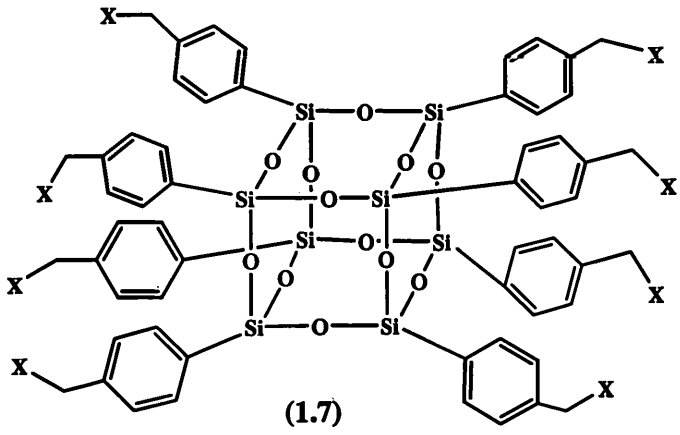
Scheme 1.4

More recently, Feher and co-workers have reported[12] that octabenzyl, *m*-tolyl and 3,5-methylphenylsilsesquioxanes can be obtained in a good yield (22-25%) by hydrolysis of the corresponding trichlorosilane in ethanol. The reaction involved carefully adding trichlorosilanes, $RSiCl_3$, (R = benzyl, *m*-tolyl and 3,5-methylphenyl) to well stirred ethanol at room temperature. The mixture was then refluxed for 2-3 days, as shown in Scheme 1.5. Octasilsesquioxanes were obtained by precipitation from the concentrated reaction

mixture, which could then be recrystallised from a mixed solvent of dichloromethane, acetone and methanol. Subsequently, they found[13] that (*p*-chloromethyl)phenyltrichlorosilane could be condensed hydrolytically to give the corresponding octasilsesquioxane **1.6**. The procedure was much simpler, and involved refluxing (*p*-chloromethyl)phenyltrichlorosilane in an acetone/water solution.



Scheme 1.5

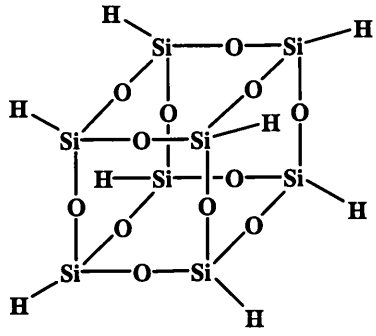


a X = I
b X = OH
c X = ONO_2
d X = OAc
e X = $O(COC_6H_4NO_2)$
f X = $O(COC_6H_4CO_2Me)$

Although the yield was low (6-15%), octasilsesquioxane **1.6** was found to be a synthetically useful precursor for other functionalised octasilsesquioxanes. They showed that the eight chlorines in octasilsesquioxane **1.6** could be quantitatively replaced by iodine by refluxing with sodium iodide for 10 hours to give the octasilsesquioxane **1.7a**. They found that octasilsesquioxane **1.7a** was an excellent precursor to highly functionalised

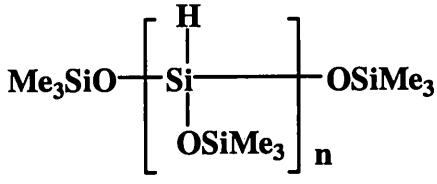
silsesquioxanes, such as octasilsesquioxane **1.7b-f**, $(p\text{-}XCH_2C_6H_4SiO_{3/2})_8$, where X is OH, ONO_2, OAc, *p*-nitrobenzoyl and methylterephthaloyl.

Another important silsesquioxane, octahydrosilsesquioxane **1.8**, T_8H_8, was investigated at the same time, and also found to be a useful precursor to functionalised silsesquioxanes.



(1.8)

The first reported isolation of T_8H_8 **(1.8)** was by Muller and co-workers in 1959.[14] They obtained approximately a 0.2% yield of T_8H_8 **(1.8)** as a by-product in the reaction of trichlorosilane with 80% sulphuric acid in the presence of hexamethyldisiloxane, which they were using to prepare a linear polysilsesquioxane **1.9**.



(1.9)

They found T_8H_8 **(1.8)** to be crystalline and soluble in hexane and benzene. On the basis of molecular weight and other analytical data, Muller suggested that the T_8H_8 **(1.8)** species should have a cubic structure. This was subsequently confirmed by Larsson[8] using single crystal X-ray crystallography in 1960.

Ten year later, Frye and co-workers reported[15] a relatively high yielding route for the

preparation of T_8H_8 **(1.8)**, as well as other lower and higher molecular weight silsesquioxane cages. The reaction involved the slow addition of a trichlorosilane solution in benzene to a stirred solution of concentrated sulphuric acid in benzene, as shown in Scheme 1.6.

$$HSiCl_3 \xrightarrow[\text{Benzene}]{H_2SO_4} \underset{\text{Volatile}}{(HSiO_{3/2})_{8\text{-}16}} + \underset{\text{Nonvolatile}}{(HSiO_{3/2})_{n>16}}$$

Scheme 1.6

The mixture initially produced small quantities of water from the reaction of benzene and H_2SO_4, as shown in Scheme 1.7.

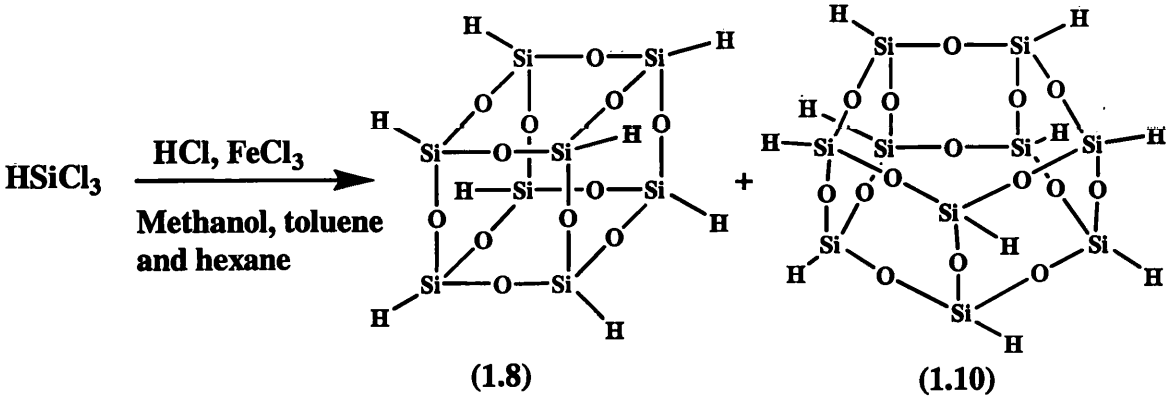
$$H_2SO_4 + C_6H_6 \longrightarrow C_6H_5SO_3H + H_2O$$

Scheme 1.7

This "scarce-water" then hydrolytically condensed the trichlorosilane, $HSiCl_3$, to give 99% of soluble decasilsesquioxanes, $T_{10\text{-}16}R_{10\text{-}16}$ cages. However, only a trace of T_8H_8 **(1.8)** was identified. Frye and co-workers found that T_8H_8 **(1.8)** could be prepared by adding a solution of trimethoxysilane, $HSi(OMe)_3$, in cyclohexane to a cyclohexane solution of acetic acid (previously saturated with anhydrous hydrochloric acid). The T_8H_8 **(1.8)** was isolated in approximately 13% yield.

Recently, Agaskar described[16] a new synthetic route for the synthesis of T_8H_8 **(1.8)** giving a high yield (17.5%) of the crystalline cage, Scheme 1.8. The reaction uses a partially hydrated metal salt solution to create "scarce water". A trichlorosilane solution in hexane was added very slowly over a period of 9 hours to a mixture of iron chloride, concentrated hydrochloride acid, methanol, toluene and hexane. The hexane solution was neutralised and dried by potassium carbonate and calcium chloride to give a mixture of T_8H_8 **(1.8)** and

decahydrosilsesquioxane **1.10**, $T_{10}H_{10}$. T_8H_8 **(1.8)** was very easily purified by washing with hexane.



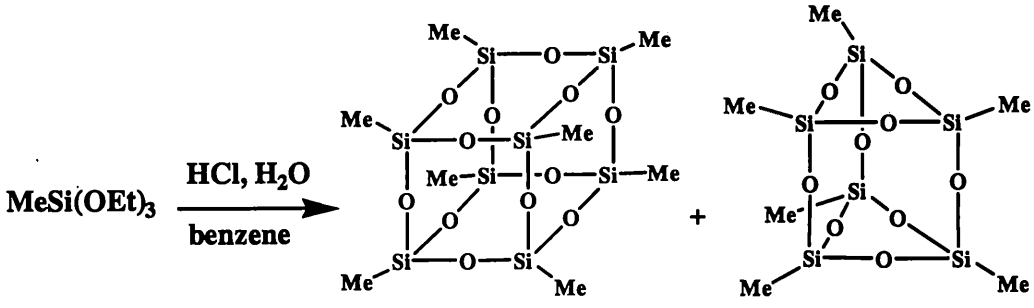
Scheme 1.8

Subsequently, Bassindale and Gentle modified Agaskar's procedure by reducing the reaction time to 5.5 hours using a peristaltic pump.[17] A 11.8% yield of T_8H_8 **(1.8)** as needle shaped crystals, was obtained from recystallisation of the reaction residue from hexane. They also investigated a new efficient route to functionalise T_8H_8 **(1.8)** cages, whereby the Si-H on the core was used to hydrosilylate a variety of alkenes to give a range of functionalised octasilsesquioxanes. This hydrosilylation will be discussed later in section 1.2.4.1.

1.2.2.2 Hydrolytic condensation of alkyltrialkoxysilanes, $RSi(OR)_3$

Alkyltrialkoxylsilanes are another trifunctional monomer, which can be used in the synthesis of octasilsesquioxanes. The first report of the synthesis of an octasilsesquioxane from an alkytrialkoxysilane was by Sprung and Guenther in 1955.[2] They found that the hydrolysis of methyltriethoxysilane in benzene with hydrochloric acid gave octamethylsilsesquioxane **1.2** as a by-product and hexamethylsilsesquioxane **1.1**, as shown in Scheme 1.9. The condensation process was rather complex. They found that the nature of the condensation product was affected by the amount of water, the time for reaction, the catalyst and the solvent system. Hydrolysis of methyltriethoxysilane in benzene with three

equivalents of water gave volatiles, which contained 6 or 8-membered polysiloxane rings. A longer time for this hydrolysis led to a decrease in the yield of volatiles. Under the same conditions, hydrolysis without an acid catalyst resulted in the formation of more resin and less distillable volatiles. When the solvent system was changed to an alcohol solution, hydrolysis of methyltriethoxysilane with three equivalents of water gave an insoluble methylsilicone gel as the sole product. However, the product turned out to be a disiloxane on reducing the amount of water. They found that octamethylsilsesquioxane **1.2** could be obtained by partial hydrolysis of methyltriethoxysilane in benzene with water, and hexamethylsilsesquioxane **1.1** could be obtained from hydrolysis of methyltriethoxysilane in benzene with water by standing at room temperature for a few weeks.



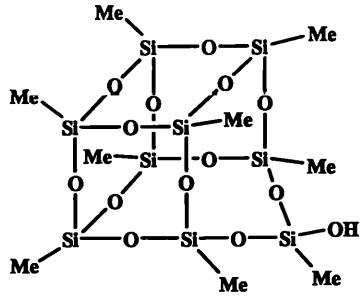
(1.2) (1.1)

Scheme 1.9

Subsequently, Sprung and Guenther reported[3] that hexa and octaethylsilsesquioxane cages could be obtained by distillation of the hydrolysis product obtained with three molar equivalents of water. They found that the best method was to co-hydrolyse equimolar quantities of ethyltrichlorosilane and ethyltriethoxysilane in benzene with two equivalents of water.

Sprung and Guenther also demonstrated[18] that hydrolysis of methyltri-*iso*-propoxysilane in benzene with three moles of water, using hydrochloric acid as a catalyst, gave a gel-like resin. When a higher concentration of methyltri-*n*-butoxysilane and catalyst were used, a

new silsesquioxane cage **1.11,** MeT_9OH, was obtained from the hydrolysis product mixture.



(1.11)

Again, they found that the yield of octamethylsilsesquioxane **1.2** obtained from the hydrolysis of methyltributoxysilane was affected by the solvent system and catalyst used. Using a ten fold excess of hydrochloric acid catalyst and a longer reaction time, only a very small amount of **1.2** was obtained. Stirring methytri-*n*-butoxysilane with cold water for two months, followed by hydrolysis in benzene gave a 5% yield of **1.2**. The yield of **1.2** could be increased up to 9% by using *iso*-butyl methyl ketone as the solvent and a ten fold excess of hydrochloric acid catalyst.

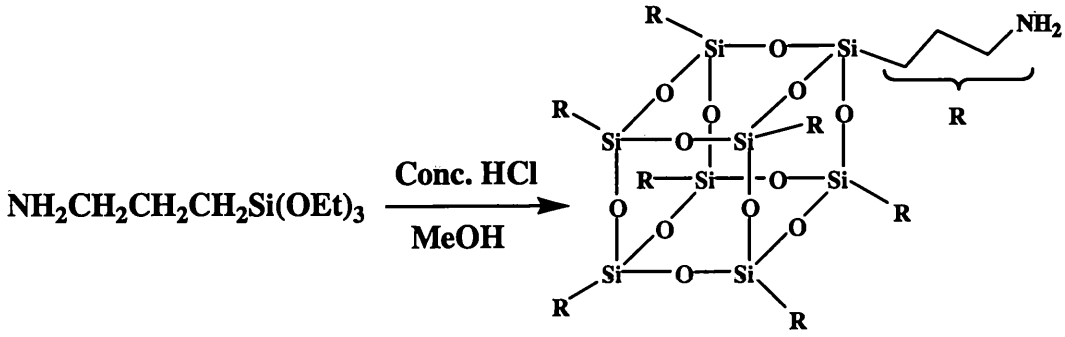
Sprung and Guenther made no attempt to explain the reaction mechanisms of these hydrolyses of alkytrialkoxysilanes.[19] However, they later speculated on the hydrolytic condensation mechanism of amyltriethoxysilane and phenyltriethoxysilane based on the IR spectra and sublimation temperature of the solid obtained from precipitation of the reaction mixture, using either an acid or alkali catalyst, albeit under different conditions. They demonstrated that hydrolysis of amyltriethoxysilane using hydrochloric acid as the catalyst, gave volatile polysiloxanes with a molecular weight of about 1000, but no octasilsesquioxane. However, when an alkali catalyst ammonium hydroxide was employed, octaamylsilsesquioxane was obtained. The hydrolysis of phenyltriethoxysilane in *iso*-butyl methyl ketone, using hydrochloric acid as catalyst, gave a ladder-like

silsesquioxane. In the same solvent system, the hydrolysis of phenyltriethoxysilane with the alkali catalyst, tetraethylammonium hydroxide, gave octaphenylsilsesquioxane as the major product.

Brown and Vogt reported[20] that the hydrolysis of methyltriethoxysilane gave hexamethylsilsesquioxane, octamethylsilsesquioxane, silsesquioxane cage (MeT_9OH), decasilsesquioxane and dodecasilsesquioxane using potassium hydroxide as the catalyst and methanol as the solvent. The silsesquioxane cages were obtained by fractional sublimation. They subsequently reported that octacyclohexylsilsesquioxane could be synthesised by hydrolysis of cyclohexyltriethoxysilane in *iso*-butyl ketone using tetraethylammonium hydroxide as the catalyst. If the hydrolysis was carried out at a higher temperature, by refluxing the reaction mixture for 8 hours followed by standing at room temperature for 6 days, then the yield of octacyclohexylsilsesquioxane increased to 75%.

Thirty years later, Bonhomme and co-workers reported[21] that octavinylsilsesquioxane could be prepared by the hydrolysis of vinyltriethoxysilane with an acid catalyst, hydrochloric acid (0.1 M solution in water), without any solvent. Crystalline octavinylsilsesquioxane precipitated out after several days standing at room temperature. The octavinylsilsesquioxane was characterised using NMR and single crystal X-ray crystallography.

Recently, Feher and co-workers reported that an aminosilsesquioxane was obtained from the hydrolysis of 3-aminopropyltriethoxysilane, Scheme 1.10. The reaction involved hydrolysis of 3-aminopropyltriethoxysilane in concentrated hydrochloric acid with methanol to yield 30% of octaaminopropylsilsesquioxane **1.12**. The amino functionalised silsesquioxanes provide a scaffold for the elaboration of polypeptide chains and carbohydrate chains.[22,23,24,25]



(1.12)

Scheme 1.10

Subsequently, Scheider and co-workers examined[26] the hydrolysis of aryltrialkoxysilane, $ArSi(OR)_3$, (Ar = phenyl, benzyl and phenylethyl and R = methyl and ethyl) using a range of different catalysts and temperatures. They found that phenyl, benzyl and phenylethyltrialkoxysilane polymerised to form high molecular weight, soluble polysilsesquioxanes, which could be analysed using NMR and GPC.

In summary, the hydrolytic condensation of trifunctional monomers gives rise to a wide range of interesting products, including complex resins, T-gels, cross-linked three-dimensional networks, ladder-type and cage-like silsesquioxanes, such as T_6R_6, T_8R_8, $T_{10}R_{10}$ and $T_{12}R_{12}$. The mechanism of these hydrolytic polycondensations is a multistep and rather complicated process. The reaction rate, the degree of oligomerisation and the yield of the final silsesquioxane are all dependent upon a number of factors, such as:

a) The concentration of the initial silane, $RSiX_3$

b) The nature of the solvent

c) The nature of R, the substituent on the silane, $RSiX_3$

d) The nature of the functional group X of $RSiX_3$

e) The type of catalyst

f) The temperature

g) The addition of water

h) The solubility of the polyhedral silsesquioxanes that are formed

The influence of these factors has been studied, both individually and together, without any quantitative estimation of their effect on the outcome of the reaction. However, the observed behaviour can be qualitatively explained by the complicated nature of the polycondensation process and the interdependence of the above factors. Despite the complexity, many hydrolytic condensation reactions produce synthetically useful quantities of fully condensed polysilsesquioxane frameworks containing 6, 8,10, and 12 Si atoms, such as T_6R_6, T_8R_8, $T_{10}R_{10}$ and $T_{12}R_{12}$ cages.

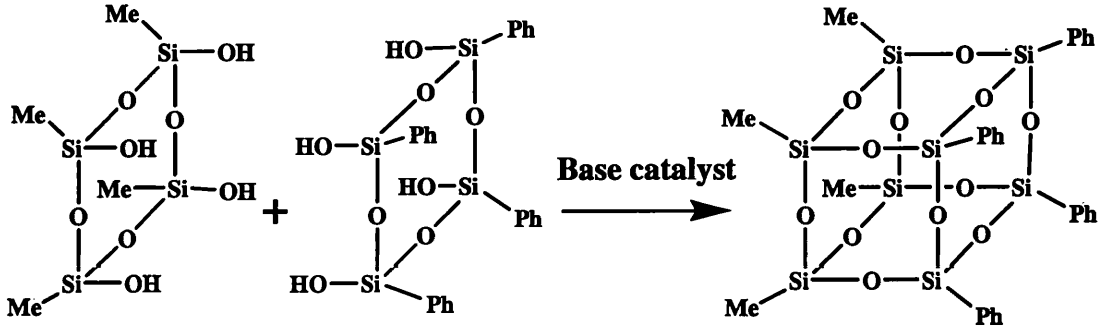
In spite of its time-consuming nature, the synthesis of silsesquioxanes using hydrolytic condensation has remained one of the most universal and traditional synthetic pathways to polysilsesquioxanes and their homo derivatives. Table 1.2 summarises the silsesquioxane cages that have been prepared from trifunctional monomers.

Table 1.2 Selected Polyhedral Silsesquixoanes Synthesised from $RSiX_3$

$RSiCl_3$ or $RSi(OEt)_3$	Product $(RSiO_{3/2})_n$, n =	Yield (%)	Ref.
$HSiCl_3$	8/10	6-20	15-17
$MeSiCl_3$	8/10/12	37	4
$VinylSiCl_3$	8	20-49	27
$EtSiCl_3$	8	37	4
$AllySiCl_3$	8	7-13	11
n-$PrSiCl_3$	8	44	4
$^{i}PrSiCl_3$	8	17	28
n-$BuSiCl_3$	8	38	4
c-$C_6H_{11}SiCl_3$	6/8	10-20	4, 7, 29, 30
$PhSiCl_3$	8	9-25	6
m- $MeC_6H_4SiCl_3$	8	25	13
$PhCH_2SiCl_3$	8	31	13
p-$ClCH_2C_6H_4SiCl_3$	8	<15	12
3,5-$Me_2C_6H_3SiCl_3$	8	22	13
$C_6H_5Si(OEt)_3$	8	-	19
$MeSi(OEt)_3$	6/8	-	2, 18, 20
$EtSi(OEt)_3$	6/8	-	3
$VinylSi(OEt)_3$	8	-	21
$AmylSi(OEt)_3$	8	-	19
$HS(CH_2)_3Si(OEt)_3$	8	17	31
$Cl(CH_2)Si(OMe)_3$	8	25	31
$H_2N(CH_2)_3Si(OEt)_3$	8	30	22
t-$ButylSiCl_3$	6	25	32
$ThexylSiCl_3$	6	41	32

1.2.2 Condensation of Si-functionalised oligocyclosiloxanes, $(RXSiO_{2/2})_n$

Andriano first carried out[33] the condensation of silicon-functionalised cyclosiloxanes to give octasilsesquioxanes. 1,3,5,7-tetramethylcyclotetra-siloxanol **1.13** and 1,3,5,7-tetraphenylcyclotetra-1,3,5,7-siloxanol **1.14** were reacted together in the presence of a basic catalyst in ether to form silsesquioxane cage **1.15**, as shown in Scheme 1.11.



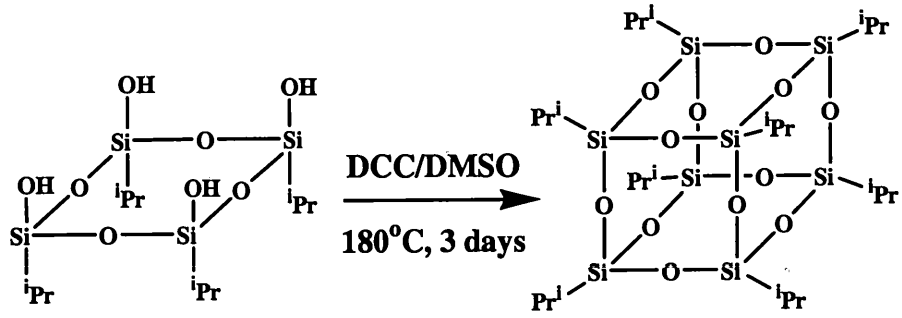
(1.13) **(1.14)** **(1.15)**

Scheme 1.11

The yield of the product was dependent upon the concentration of the initial siloxanol. The maximum yield was as high as 95% when very low concentrations of siloxanol (2.5%) were employed. Later the syntheses of silsesquioxane cages, $(RSiO_{3/2})_n$, (R = methyl and ethyl) where n = 4, 6, and 8, were reported using an organic solvent in the presence of potassium hydroxide as a catalyst. The condensation products again depended on the reaction conditions giving either polyhedral silsesquioxanes or high molecular weight ladder-like silsesquioxanes.

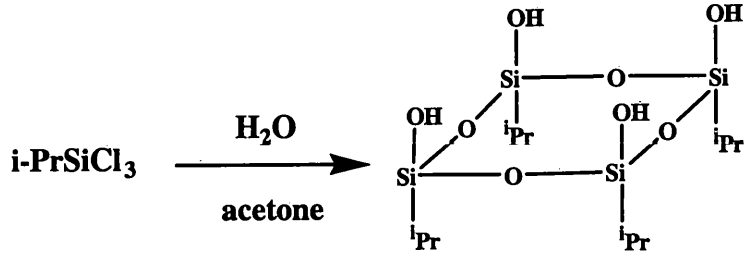
More recently, Unno and co-workers have reported[28] that octa-*iso*-propylsilsesquioxane **1.17**, $^{i}PrT_8$, can be synthesised in high yield (45%) by coupling two 1,3,5,7-tetra-*iso*-propylcyclotetra-1,3,5,7-siloxanol **1.16** units using a mixture of DCC and DMSO, as shown in Scheme 1.12.[34] The 1,3,5,7-tetra-*iso*-propylcyclotetra-1,3,5,7-siloxanol **1.16** could be synthesised using two methods. The first was the hydrolysis of *iso*-

propyltrichlorosilane in water/acetone with careful control of the reaction conditions, to yield 1,3,5,7-tetra-*iso*-propylcyclotetra-1,3,5,7-siloxanol **1.16** in 20% yield. The reaction involved the addition of *iso*-propyltrichlorosilane to water at 0°C for 30 minutes followed by stirring at 0°C for 21 hours and then for five days at room temperature, as shown in Scheme 1.13.[28]



(1.16) **(1.17)**

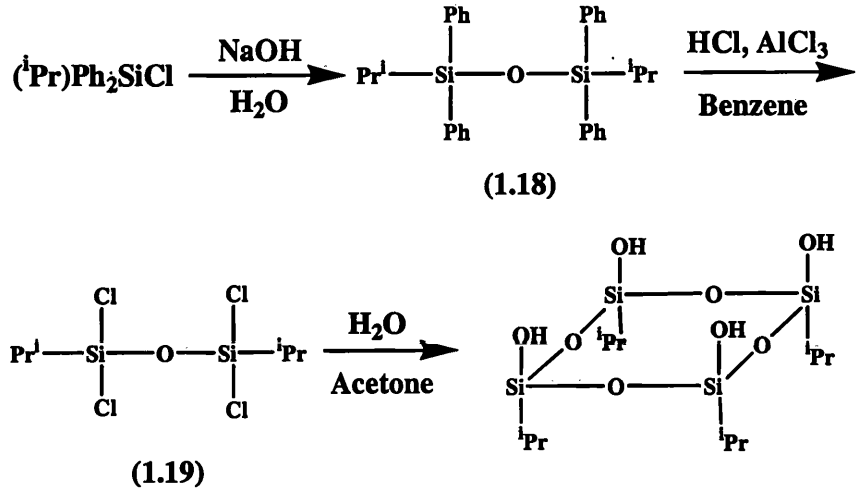
Scheme 1.12



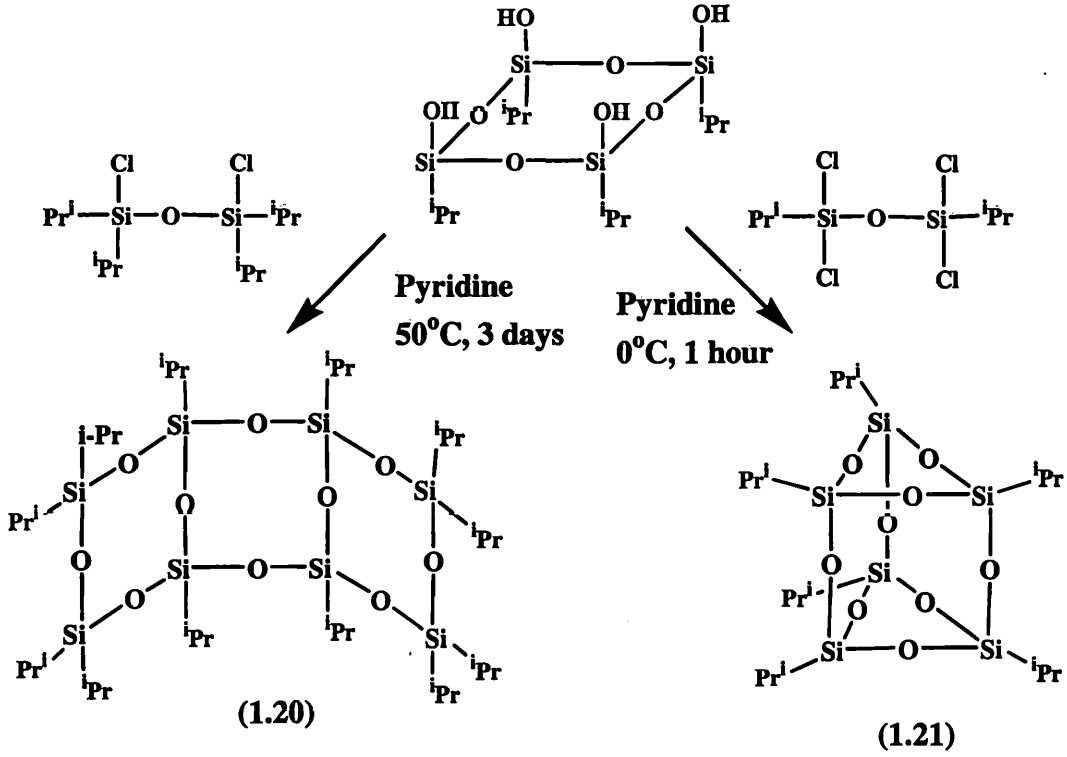
Scheme 1.13

The second route was a three step reaction, but nevertheless, gave a very high yield (87%) of 1,3,5,7-tetra-*iso*-propylcyclotetra-1,3,5,7-siloxanol **1.16**. Chloro-*iso*-propyldiphenylsilane was employed as the starting material instead of *iso*-propyltrichlorosilane. In the first step, chloro-*iso*-propyldiphenylsilane was hydrolysed to di-*iso*-propyltetraphenyldisiloxane **1.18** by refluxing with sodium hydroxide in water. This disiloxane **1.18** was then reacted with hydrogen chloride gas in the presence of aluminium chloride in benzene to yield 96% of 1,1,3,3-tetrachloro-1,3-di-*iso*-propyldisiloxane **1.19**.

The final step was hydrolysis of this product by adding to water/acetone at 0°C for 30 minutes and further stirring at 0°C for 12 hours and 4 days at room temperature to give 46% yield of 1,3,5,7-tetra-*iso*-propylcyclotetra-1,3,5,7-siloxanol **1.16** as shown in Scheme 1.14.



Scheme 1.14

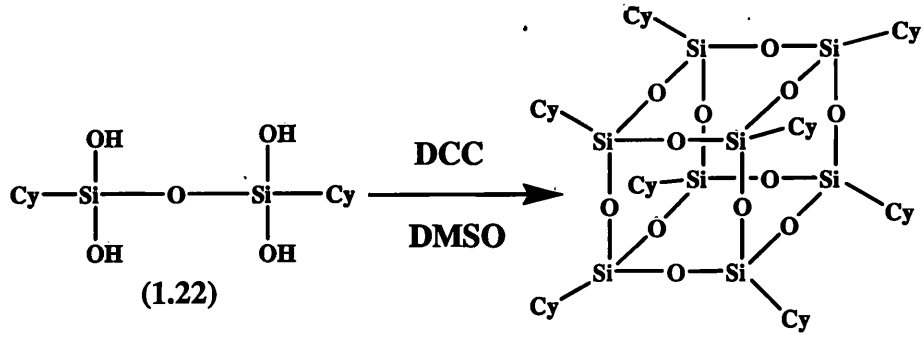


Scheme 1.15

They also demonstrated that the condensation of 1,3,5,7-tetra-*iso*-propylcyclotetra-1,3,5,7-siloxanol **1.16** in the presence of dichloro-disiloxane or tetrachloro-disiloxane could form a low molecular weight ladder **1.20** or hexasilsesquioxanes **1.21**, as shown in Scheme 1.15.

1.2.2.1 Condensation of disiloxane tetrols, $[R_2Si(OH)_2]_2O$

Unno and co-workers synthesised[35] octacyclohexylsilsesquioxane, CyT_8, by the condensation of disiloxane tetrols using dehydrating reagents. 1,3-dicyclohexyldisiloxane-1,1,3,3-tetrol **1.22** was reacted with a mixture of DCC and DMSO at 120°C to give a fully condensed CyT_8 **1.23** in relatively high yield (13%), Scheme 1.16.



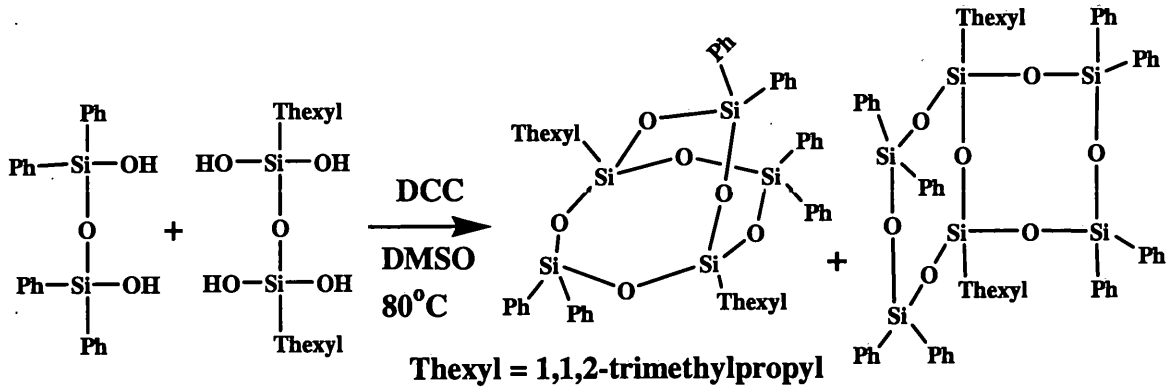
(1.22) **(1.23)**

Scheme 1.16

In a study of the condensation of disiloxane tetrols, ladder structures of silsesquioxanes have been prepared by the reaction of 1,1,3,3-diphenyldisiloxane-1,3-diol **1.24** and 1,1,3,3-dithexyldisiloxane-1,1,3,3-tetrol **1.25** with a 1:1 mixture of DCC and DMSO at 80°C in yields of 24% **1.26** and 17% **1.27**, as shown in Scheme 1.17.

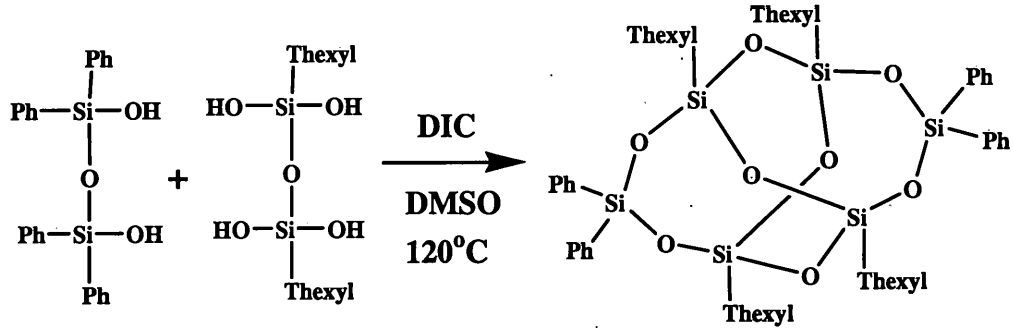
Ladder-like silsesquioxane **1.26** was the only product isolated in the condensation reaction of disiloxanediol and disiloxanetetrol with DIC at 120°C for 7 days. However, the same starting material with DIC, using a shorter reaction time (3 days), Scheme 1.18, gave only a bicyclic ladder structure product **1.28** with no evidence of the formation of ladder-like silsesquioxane **1.26** and **1.27**. These ladder-like silsesquioxanes **1.27** and **1.28** were fully

characterised by NMR and single crystal X-ray crystallography.



(1.24) (1.25) (1.26) (1.27)

Scheme 1.17



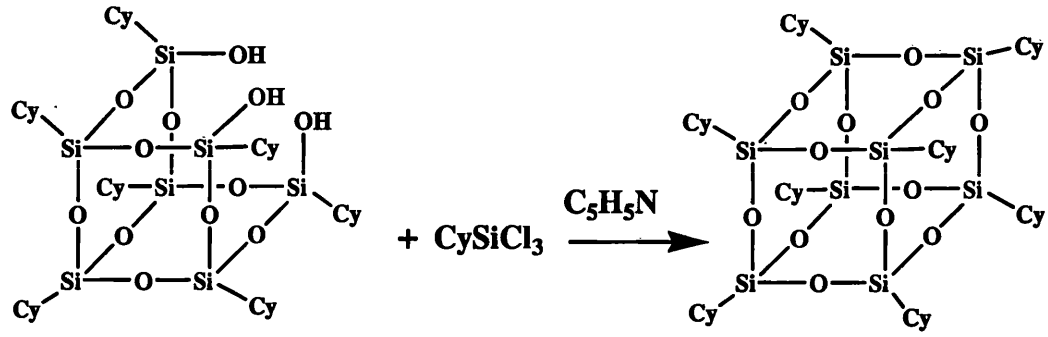
(1.28)

Scheme 1.18

1.2.2.2 Condensation of siloxanetriols, $(R_7SiO_{3/2})_7(OH)_3$

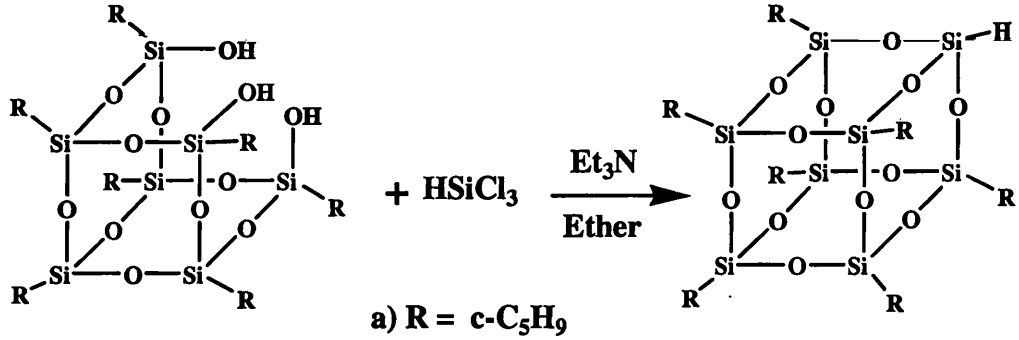
The first condensation of a siloxanetriol was described by Brown[7] and involved the reaction of $CyT_7(OH)_3$ **1.29** with cyclohexyltrichlorosilane to form octacyclohexylsilsesquioxane **1.23**, CyT_8, as shown in Scheme 1.19. This type of condensation of $CyT_7(OH)_3$ **1.29** has been well characterised by Feher and co-workers.[36] They also reported that $R_7T_7(OH)_3$, (R = cyclohexyl, cyclopentyl), reacted with trichlorosilane to afford a heterosilsesquioxane cage **1.32**, $R_7H(SiO_{3/2})_8$, by adding freshly distilled trichlorosilane to a solution of $R_7T_7(OH)_3$ and triethylamine in diethylether. The reaction mixture was stirred overnight, then filtered to remove triethylammonium chloride

to give the product **1.30** in 88% yield after removal of solvent, as shown in Scheme 1.20.[36]



(1.29)

Scheme 1.19



a) R = c-C_5H_9
b) R = c-C_6H_{11}

(1.30)

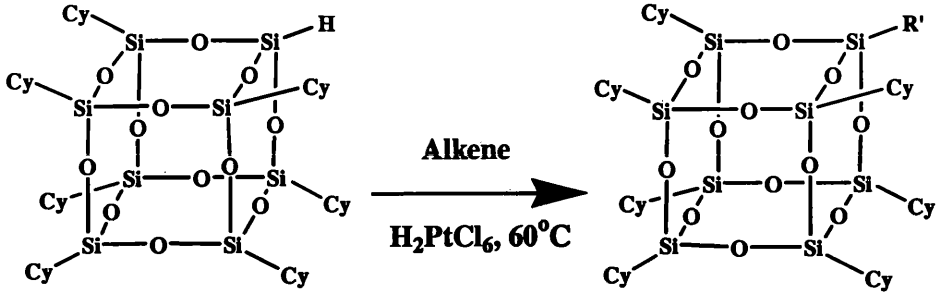
Scheme 1.20

This reaction has been explored recently using different trichlorosilanes, $RSiCl_3$, to give a wide range of heterosubstituted silsesquioxane cages, as shown in Table 1.3.

Table 1.3 Selected Heterosubstitution Silsesqioxanes

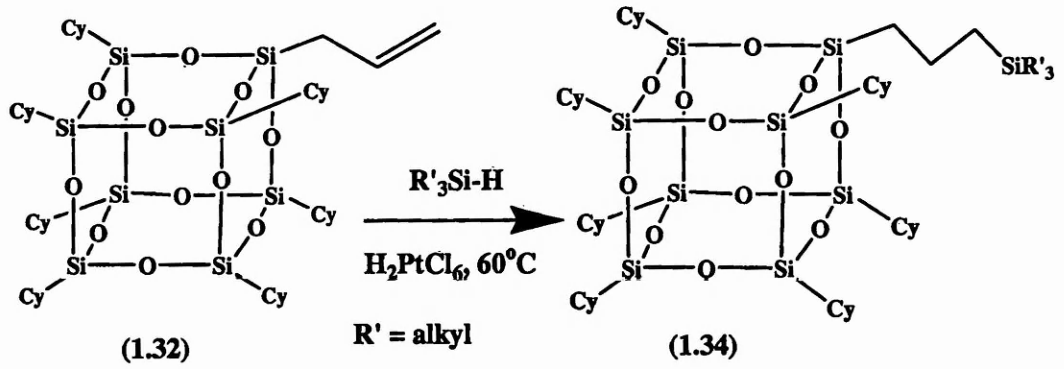
$R_7R'(SiO_{3/2})_8$, R =	R' =	Yield, (%)	Ref.
c-C_6H_{11} or c-C_5H_9	H	48-90	36, 37
c-C_6H_{11}	Cl	86	38
c-C_6H_{11}	OH	-	39
c-C_6H_{11}	$OSiMe_2H$	98	37
c-C_6H_{11}	$CH_2=CH_2$	82	37
c-C_6H_{11}	$CH_2CH_2=CH_2$	89	37
c-C_6H_{11}	$(CH_2)_6CH=CH_2$	92	37
c-C_6H_{11}	C_6H_5	-	40
c-C_6H_{11}	$C_7H_9CH_2CH_2$	93	41

Furthermore, these heterosubstituted silsesquioxanes **1.31** and **1.32** provide an opportunity for the synthesis of further functionalised silsesquioxanes, for example, hydrosilylation can be used to elaborate the side chain, such as heterosubstituted silsesquioxanes **1.33** and **1.34**, even a cage polymer **1.35**, as shown in Scheme 1.21, Scheme 1.21 and Scheme 1.23.[42,43]



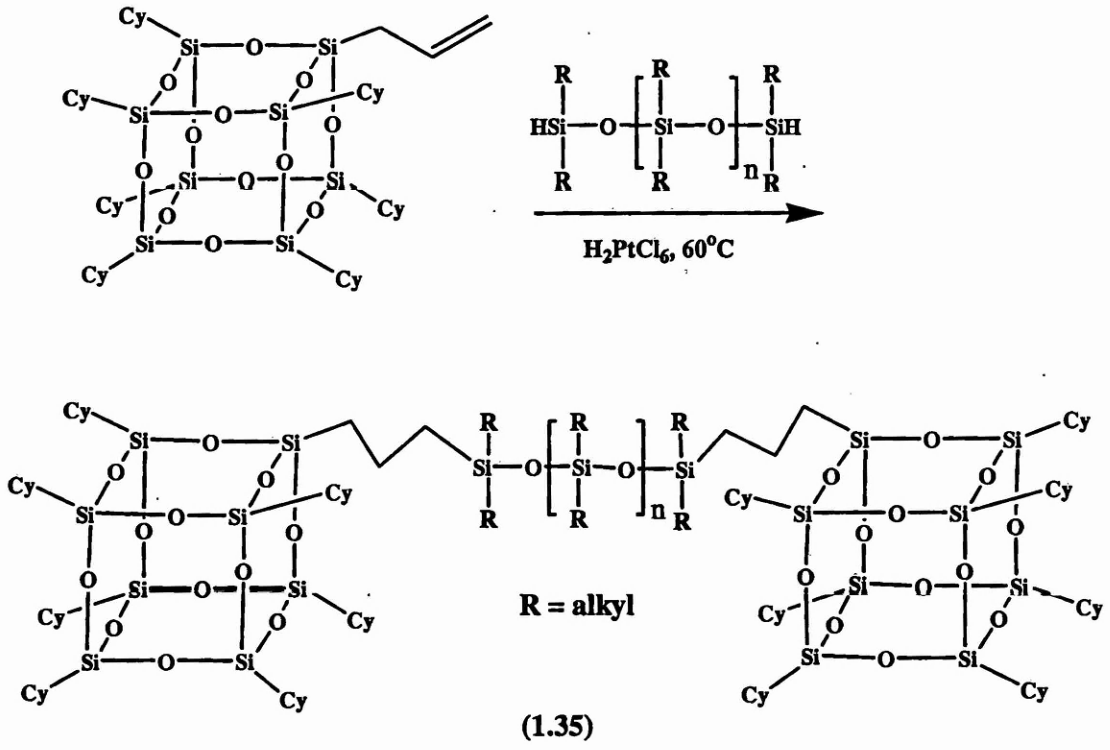
(1.31) **(1.33)**

Scheme 1.21



(1.32) (1.34)

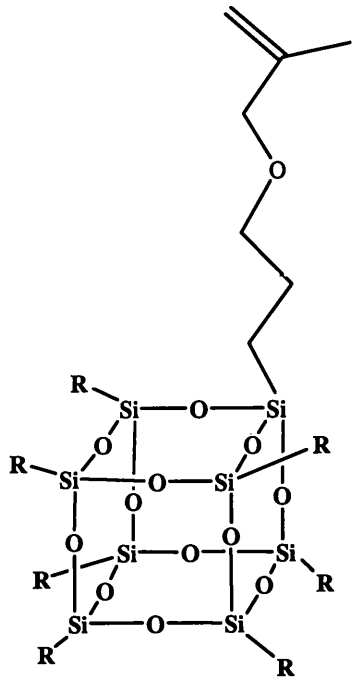
Scheme 1.22



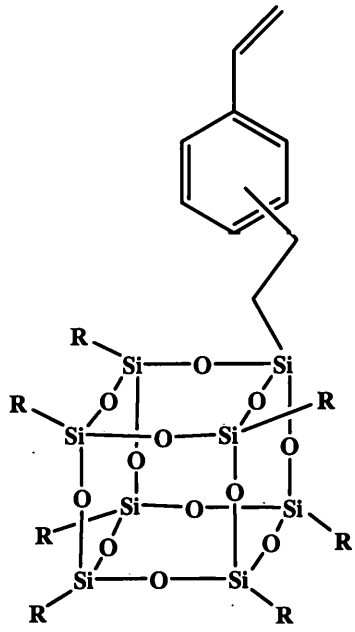
(1.35)

Scheme 1.23

Such heterosilsesquioxane cages are also useful precursors for polymers.[41,44] Lichtenhan and co-workers have demonstrated that a variety of heterosilsesquioxanes have novel properties[45,46] suitable for extensive applications as hybrid materials[47], catalysts[48] and copolymers.[49] For example, heterosubstituted silsesquioxane **1.36** and **1.37**[50] was used as a co-polymer precursor.

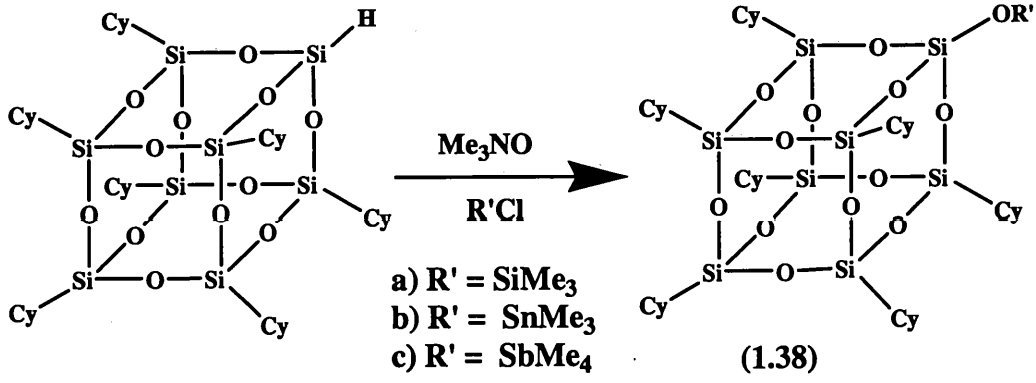


(1.36)



(1.37)

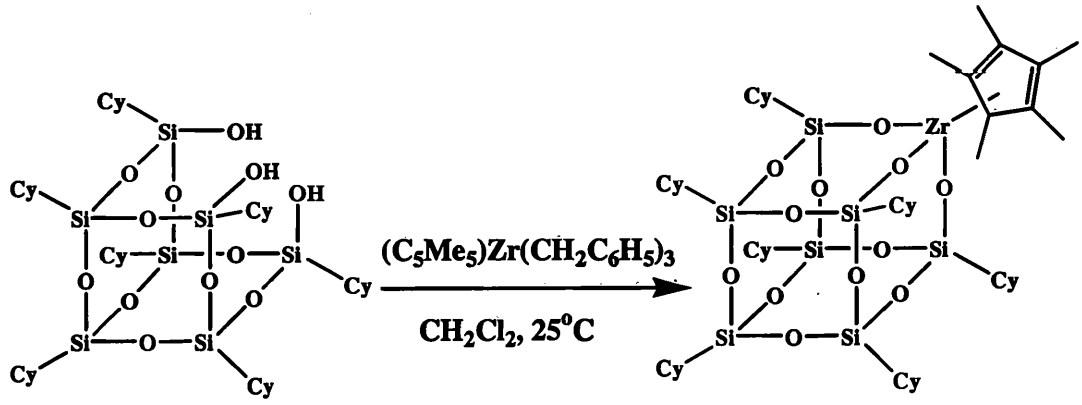
Feher and co-workers also reported that heterosubstituted silsesquioxanes **1.29**, $R_7H(SiO_{3/2})_8$, is a very useful precursor for metallosilsesquioxanes. $R_7H(SiO_{3/2})_8$ **(1.30)** was oxidised to give metallosilsesquioxanes **1.38**, $R_7OR'(SiO_{3/2})_8$, by treatment of $R_7H(SiO_{3/2})_8$ **(1.30)** with trimethylamine N-oxide (Me_3NO) and metal halides such as Me_3SiCl, Me_3SnCl and Me_4SbCl in THF and refluxed for 44 hours to give metallosilsesquioxanes **1.38** in 46-87% yield as shown in Scheme1.24.[36]



(1.38)

Scheme 1.24

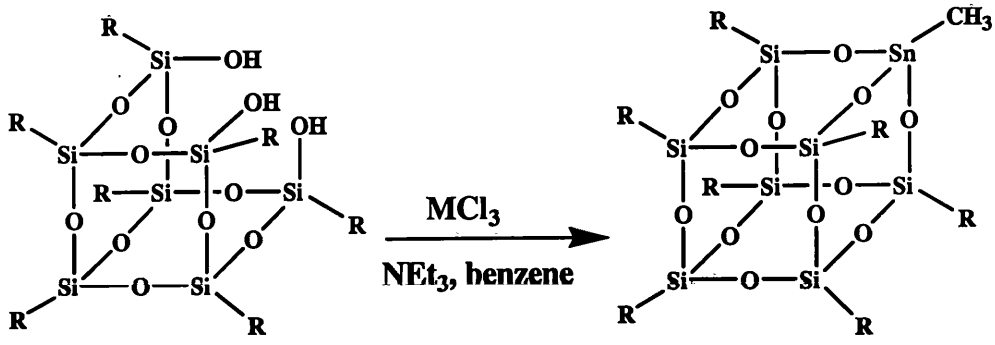
Feher and co-workers have also developed a "corner capping" method to synthesise a wide range of metallosilsesquioxanes. In 1986, they reported the first example of metallosilsesquioxanes.[51] $CyT_7(OH)_3$ **(1.29)** is very reactive and reacted with transition-metal halide and alkyl complexes, Scheme 1.25. The preparation involved reacting a 0.01 M solution of $CyT_7(OH)_3$ **(1.29)** in dichloromethane with 1 equivalent of $(C_5Me_5)Zr(CH_2C_6H_5)_3$ to afford 3 equivalents of toluene and a quantitative yield of the zirconium-containing silsesquioxane **1.39**. The Structure of silsesquioxane **1.39** was characterised by X-ray crystallography.



(1.39)

Scheme 1.25

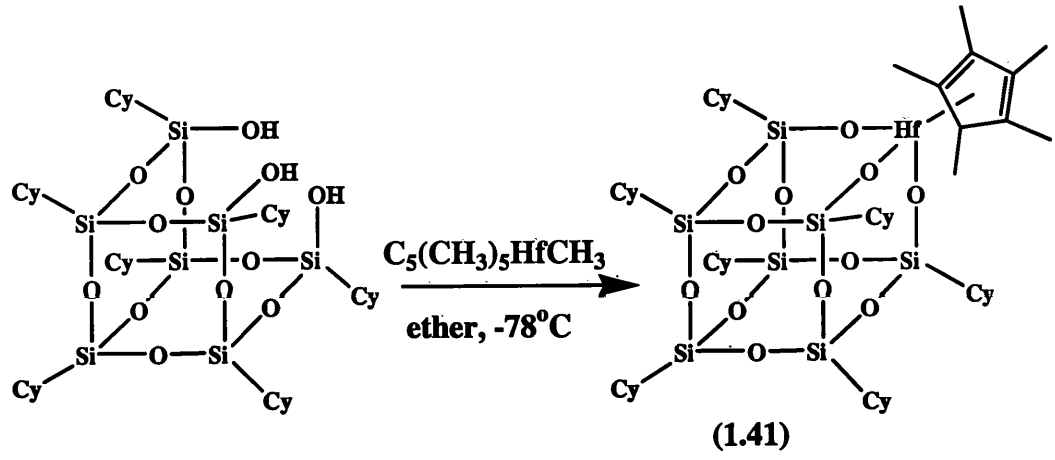
Subsequently, Feher and co-workers demonstrated that $CyT_7(OH)_3$ **(1.29)** reacted with methyltrichlorostannane to give "corner capping" products. The reaction was carried out by adding methyltrichlorostannane to a solution of $CyT_7(OH)_3$ **(1.29)** and triethylamine in benzene. The mixture was stirred for 2 hours, and then the volatiles removed. Extraction of the residue with hexane gave the metallosilsesquioxane product **1.40** in 35-74 % yield, as shown in Scheme 1.26.[52]



R = c-C_5H_9, c-C_6H_{11} M=CH_3SnCl_3 **(1.40)**

Scheme 1.26

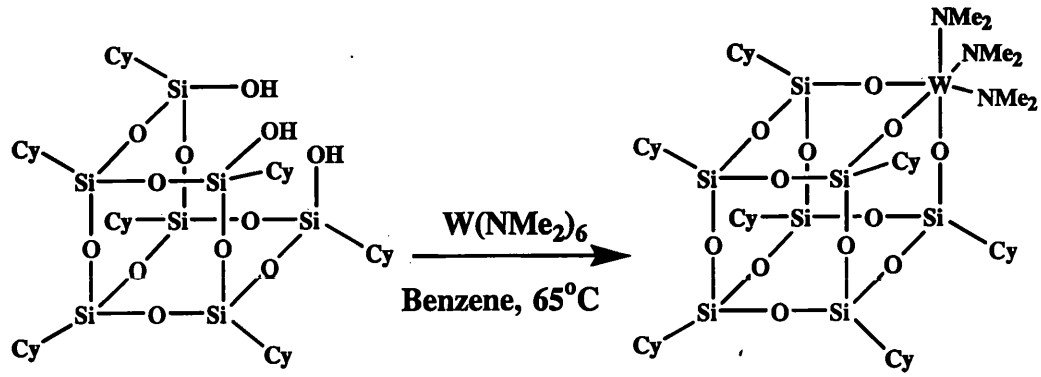
More recently, Gun'ko and co-workers reported[53] hafnium-containing silsesquioxanes could be synthesised using a similar method, as shown in Scheme1.27. $CyT_7(OH)_3$ **(1.29)** was treated with $(C_5H_5)HfMe_3$ in ether at -78°C to produce the metallosilsesquioxane **1.41.**



(1.41)

Scheme 1.27

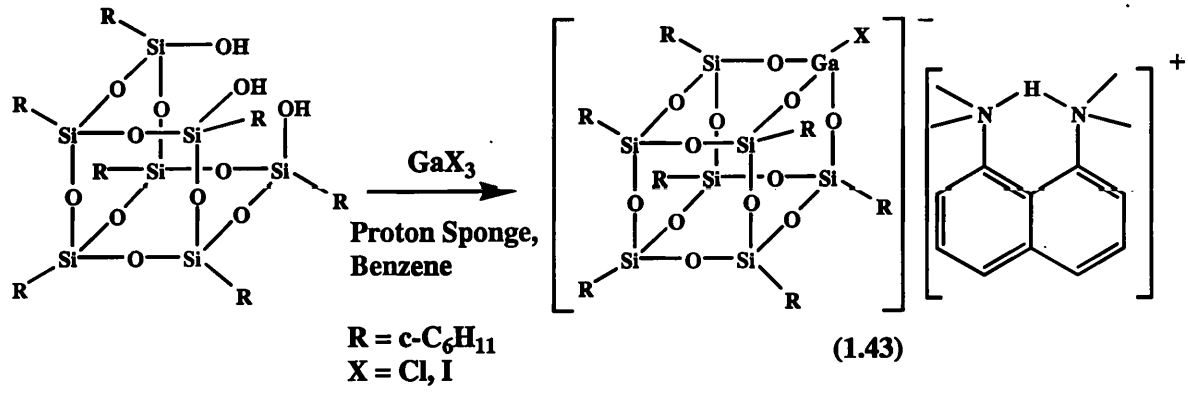
Feher and co-workers also reported that $CyT_7(OH)_3$ **(1.29)** reacted with $W(NMe_2)_3$ to afford tungsten-containing metallosilsequioxanes **1.42**, as shown in Scheme 1.28. The reaction involved stirring a reaction mixture of $CyT_7(OH)_3$ and $W(NMe_2)_6$ in benzene at 65°C for 12 hours. The solvent was removed to yield metallosilsesquioxane **1.42** in 86% yield, which was characterised by NMR and single crystal X-ray crystallography.[54]



(1.42)

Scheme 1.28

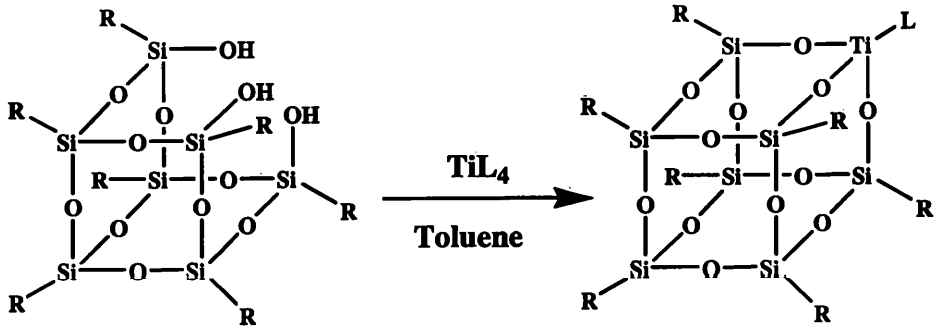
Using a similar preparation, $CyT_7(OH)_3$ (**1.29**) was also reacted with gallium trihalides, such as gallium trichloride and gallium triiodide, in benzene containing a stoichiometric amount of "Proton Sponge" to produce the corresponding gallium-containing silsesquioxane **1.43** in 58% yield, as shown in Scheme 1.29.[55]



(1.43)

Scheme 1.29

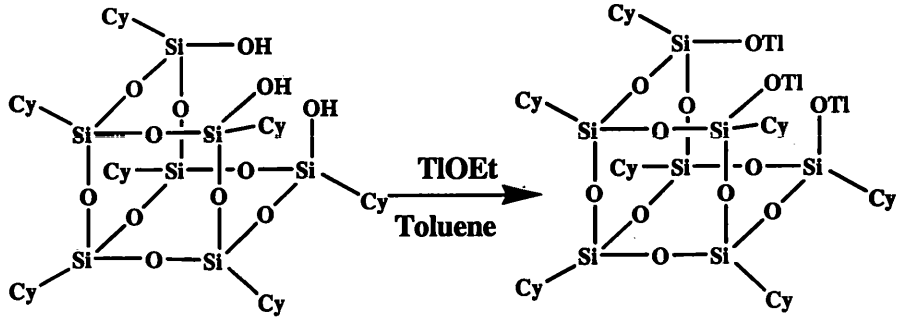
Recently, Duchateau and co-workers reported[56] that treatment of $CyT_7(OH)_3$ (**1.29**) with a cold solution (-80°C) of $Ti(CH_2Ph)_4$ in toluene gave a titanium-containing silsesquioxane **1.44** in 89% yield after removed solvent and extraction of the residue with hexane, as shown in Scheme 1.30.[56,57]



L = CH_2Ph, NMe_2, $OSiMe_3$, OPr^i **(1.44)**

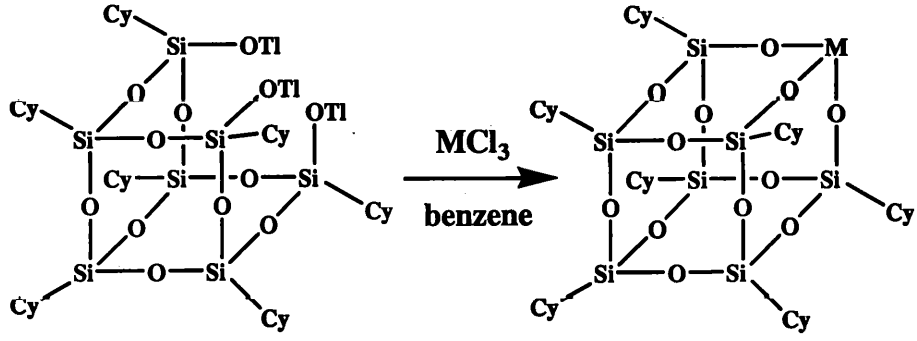
Scheme 1.30

Feher and co-workers have reported[58] that $CyT_7(OH)_3$ can be functionalised with TlOEt to give a thallium-stablilised T_7 silsesquioxide **1.45**, $CyT_7(TlO_3)$, as a useful precursor, as shown in Scheme 1.31. $CyT_7(TlO)_3$ **(1.45)** can be reacted with a variety of metal halides, such as $(C_5H_5)TiCl_3$, $MeSnCl_3$ and $SbCl_3$, to give high yield (quantified by NMR spectroscopy) of metallosilsesquioxanes **1.46**, as shown in Scheme 1.32.



(1.45)

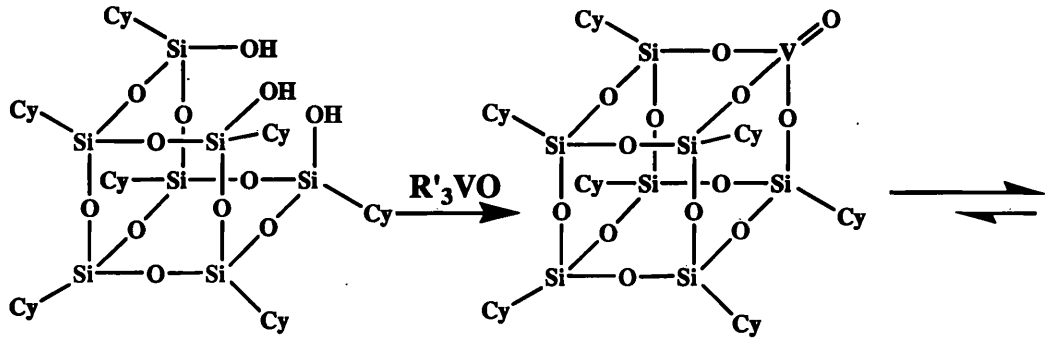
Scheme 1.31



M = C_5H_5Ti, MeSn, Sb **(1.46)**

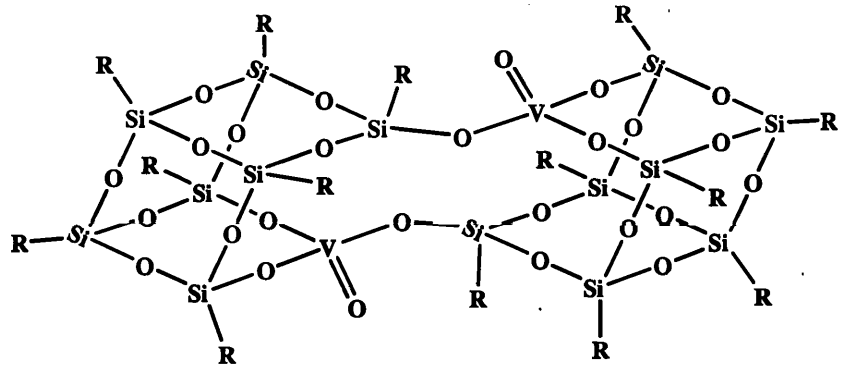
Scheme 1.32

Similarly, Feher and co-workers reported[59] that a vanadium-containing silsesquioxane **1.47** can be synthesised using $VOCl_3$, $(n\text{-}PrO)_3V{=}O$ or $(Me_3SiCH_2)_3V{=}O$, as shown in Scheme 1.33. However, in these reactions, the dimer **1.48** is thermodynamically more favourable than the single cage structure silsesquioxane.



R' = *n*-PrO, Me_3SiCH_2, Cl (1.47)

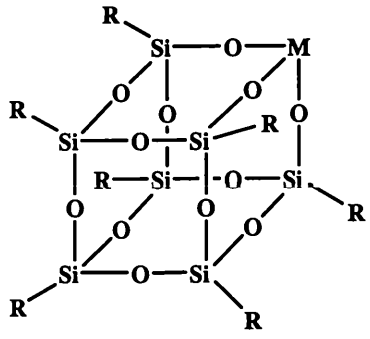
Scheme 1.33



(1.48)

In summary, $CyT_7(OH)_3$ **(1.29)** is a very useful precursor to build metal-containing heterosilsesquioxane frameworks. Table 1.4 shows the range of metallosilsesquioxanes synthesised from $CyT_7(OH)_3$.

Table 1.4 Selected Metallosilsesquioxanes



R = c-C_6H_{11}

M	Yield (%)	Ref.
$Zr(C_5Me_5)$	>90	51
Ti-X, X=CH_2Ph, OPr^i, $OSiMe_3$, NMe_3	89	60, 39
$SiMe_3$	46	36
$SnMe_3$	87	36
$SbMe_4$	83	36
$W(NMe_2)_6$	86	54
SnMe	35 -74	52, 61
V=O	>95	62, 63
GaCl	58	55
P=O	-	61
Sb	-	61

1.3.3 Co-condensation of different organosilicon trifunctional monomers

Co-condensation of two trifunctional monomers, $RSiCl_3$ or $RSi(OEt)_3$ can give heterosubstituted silsesquioxanes, Scheme 1.34.

$$RSiX_3 + R'SiX_3 \longrightarrow R_nR'_{8-n}(SiO_{3/2})_8$$

$$n = 0\text{-}8$$

Scheme 1.34

The co-hydrolysis of a mixture of trifunctional $RSiX_3$ and $R'SiX_3$ monomers usually gives a mixture of heterosubstituted oligosilsesquioxanes with all possible combinations of substituents R and R', the distribution of the substituents being of a statistical nature.

Martynova and co-workers carried out[64] the co-hydrolysis of methyl and vinyltrichlorosilanes and the products were isolated by GC and characterised by GC-MS. They found that this reaction led to nine compounds of the general formula $R_nR'_{8-n}(SiO_{3/2})_8$ with n = 0-8. They demonstrated that there were four variables that controlled the distribution of heterosilsesquioxanes, Scheme 1.35.

$$CH_3SiCl_3 + C_2H_5SiCl_3 \longrightarrow (CH_3)_n(C_2H_5)_{8-n}(SiO_{3/2})_8 \quad n=1\text{-}7$$

Scheme 1.35

The relative yields of heterosubstituted oligosilsesquioxanes with various n values depends mainly on the molar ratio and reactivity of the monomers. With an equimolar ratio of both monomers and similar rates of hydrolysis, the predominant yield compound is $R_nR'_{8-n}T_8$ with an equal number of R and R' groups, $R_4R'_4T_8$.

They also found that the yield of heterosubstituted oligosilsesquioxanes is greatly affected by the difference in the reactivity of the initial monomers. The most effective co-condensation of heterosubstituted silsesquioxanes was achieved using two trifunctional monomers that do not contain chlorine. Triacetoxysilanes were the most promising and when a particular ratio of starting materials was employed, condensation gave octasilsesquioxanes with the corresponding ratio of substituents on the core, Scheme 1.36.

$$CH_3Si(OCOCH_3)_3 + C_2H_5Si(OCOCH_3)_3 \xrightarrow{H_2O} (CH_3)_n(C_2H_5)_{8-n}(SiO_{3/2})_8 \quad n = 1\text{-}7$$

Scheme 1.36

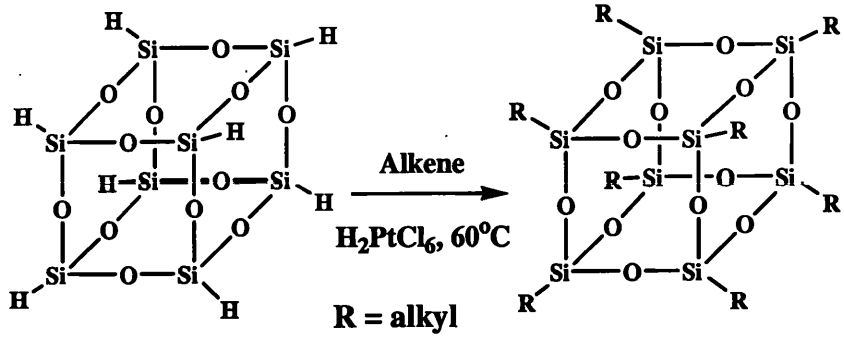
The reaction product was also affected by the time. A small distribution of substituents on the octasilsesquioxane core was achieved in a shorter time.

Heterosubstituted silsesquioxanes could also be synthesised by condensation of $R_7T_7(OH)_3$ with a wide range of $R'SiCl_3$, as mentioned previously. Another route for the synthesis of heterosubstituted silsesquioxanes is partial hydrosilylation, which will be discussed in the next section.

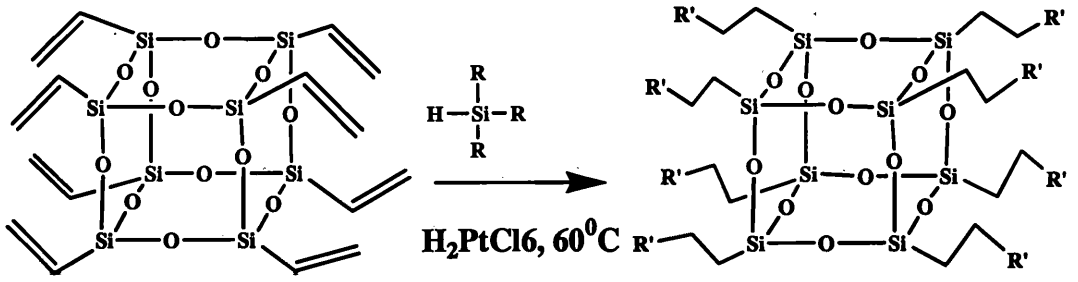
1.2.4 Reaction with retention of the silsesquioxane cages

1.2.4.1 Hydrosilylation of silsesquioxane

A great deal of work has been carried out on the preparation of functional silsesquioxane cages using reactions involving only the substituents on the silicon atoms, without affecting the skeleton of the polyhedral silsesquioxane. Hydrosilylation is one of the most important and powerful methods of generating different functionalities on the silicon atoms of silsesquioxane cages. Functionalised silsesquioxanes could be prepared by hydrosilylation of either octahydrosilsesquioxane with alkenes, Scheme 1.37 or octaalkenylsilsesquioxanes **1.49** with silanes containing Si-H to form another octasilsesquioxane **1.50**, as shown in Scheme 1.38.



Scheme 1.37



(1.49) R= alkyl, R'= SiR_3 (1.50)

Scheme 1.38

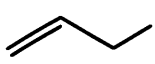
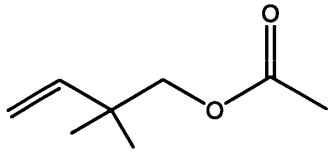
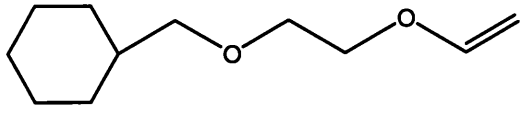
In general, this strategy can be divided into two categories depending on the extent of hydrosilylation in the product. The first category involves reactions where hydrosilylation is complete, the Si-H bond of octahydrosilsesquioxane, T_8H_8, becoming fully functionalised to give the homosubstituted silsesquioxane. The second category involves incomplete hydrosilylations to produce heterosubstituted silsesquioxanes.

a) Complete functionalisation of octahydrosilsesquioxane

Complete hydrosilylation of the eight Si-H groups of octahydrosilsesquioxane, T_8H_8, has been extensively studied and high yields of functionalised silsesquioxanes, T_8R_8, can be obtained with an appropriate catalyst. Platinum is the most common catalyst used in hydrosilylation reactions. However, the reaction often produces a mixture of α- and β-addition on the silsesquioxanes. The ratio of α and β addition is dependent on the starting materials, as shown in Table 5.

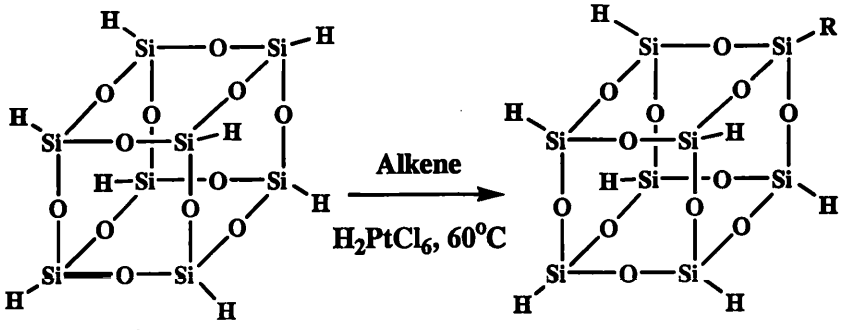
Goodby and co-workers have described the hydrosilylation of octahydrosilsesquioxane with liquid crystal mesogens to produce liquid crystal silsesquioxanes.[67,68,69]

Table 1.5 Selected Fully functionalised $(RSiO_{3/2})_8$

T_8R_8, R = Alkenes	Yield, (%)	α/β	Ref.
 X = Ph, OPh, CN, C_6H_5, $SiMe_3$, p-$MeOC_6H_4O$	>80	>95/5	31
 n = 0-8 n = 2, 4, 6, 8	>98	>95/5	17
 n = 0-8 n = 0-6	50-100	>10/1	65
	80	>99/1	22
	50-100	>10/1	66

b) Mono and multifunctionalisation of octahydrosilsesquioxane

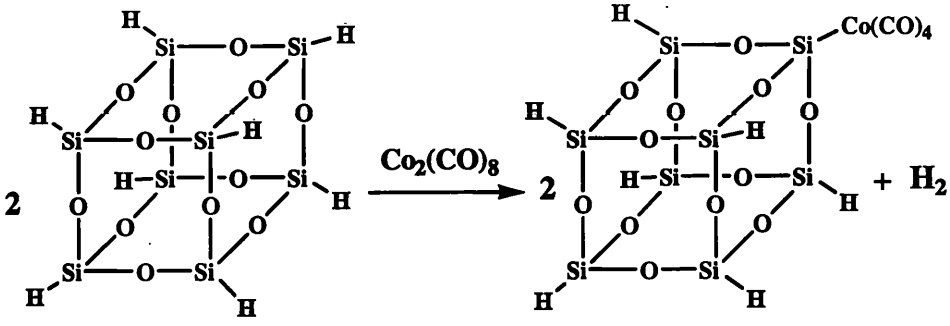
Although the partial functionalisation of octahydrosilsesquioxane, T_8H_8, usually produces a complex mixture of products, $R_nH_{8-n}(SiO_{3/2})_8$, n = 1-7,[17] monofunctionalisation can be achieved with reasonable success because the starting material has eight equivalent functional groups and is always the most abundant functional group present, providing the reaction is performed with low conversion. Calzaferri and co-workers[70,71] first reported the effective monofunctionalisation of T_8H_8 via hydrosilylation, as shown in Scheme1.39.



R = *n*-hexyl, Ph (1.51)

Scheme 1.39

The monofunctionalised silsesquioxane **1.51**, RH_7T_8, was obtained within a mixture of multifunctionalised adducts, $R_2H_6T_8$, $R_3H_5T_8$, etc.. The separation of this mixture is typically straightforward when reaction is performed with enough reagents to functionalise one Si-H group, and the expected yield is fairly low. A much better selectivity for monofunctionalisation could be achieved by functionalising the Si-H with organometallic fragments, such as $Co(CO)_4$, Scheme 1.40.[70,72,73]



(1.52)

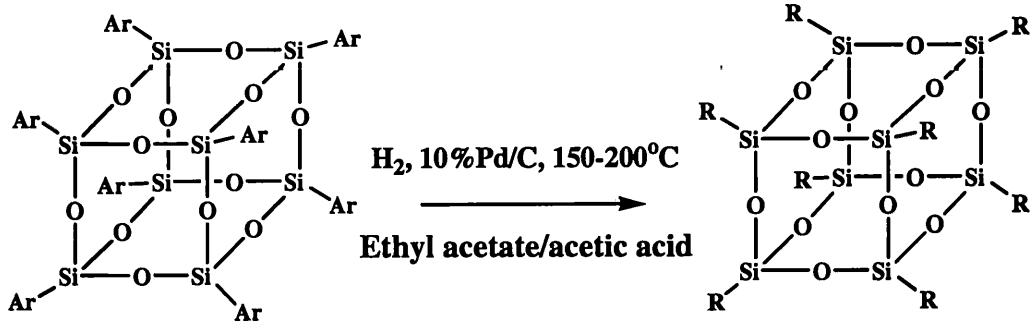
Scheme 1.40

The reaction involved treatment of T_8H_8 with octacarbonyldicobalt in toluene at 50°C under a carbon monoxide atmosphere to afford the cobalt-containing hydrosilsesquioxane **1.52**, which was characterised by NMR and single crystal X-ray crystallography.

Hydrosilylation can also be achieved via reaction of an alkenylsilsesquioxane with a compound containing an Si-H group.

1.2.4.2 Hydrogenation

Feher and co-workers have demonstrated[13] that functionality on the core can also be transformed by hydrogenation without cleavage of the Si-O-Si linkages of the silsesquioxane. Hydrogenation of an octaarylsilsesquioxane using a palladium (Pd) catalyst (10% Pd/C) in ethylacetate and acetic acid (88/12) can be achieved with prior purging (three times) of the reactor with H_2. After stirring and heating at 150-200°C, the product octaalkylsilsesquioxane was obtained, Scheme 1.41. Hydrogenation of octabenzylsilsesquioxane **1.53b** afforded virtually quantitative yields of the corresponding octacyclohexylmethylsilsesquioxane **1.54b** at 1 atm and 150°C. However, hydrogenation of other octaarylsilsesquioxanes required increased temperatures and pressures of hydrogen gas to obtain the corresponding octaalkylsilsesquioxanes. Dodecacyclohexylsilsesquioxane, CyT_{12}, was shown to be a by-product associated with the hydrogenation of octaphenylsilsesquioxane **1.53a**.



(1.53)

a) Ar = Ph
b) Ar = $PhCH_2$
c) Ar = 3-MePh
d) Ar =4-MePh
e) Ar = 3,5-Me_2Ph

(1.54)

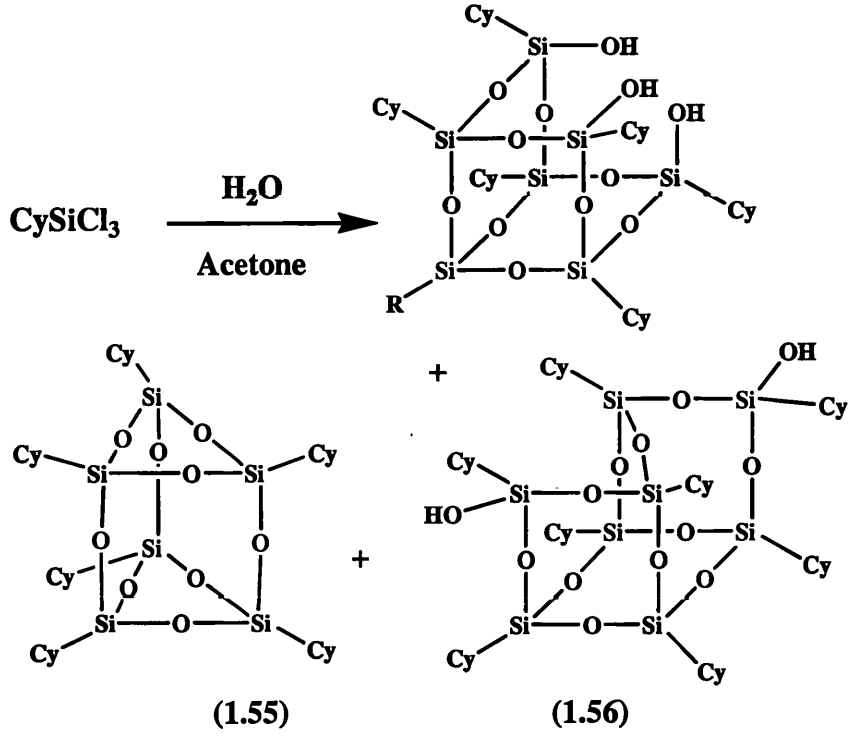
a) R = Cy
b) R = $CyCH_2$
c) R = 3-MeCy
d) R =4-MeCy
e) R = 3,5-Me_2Cy

Scheme 1.41

1.3 Hexasilsesquioxanes

Few hexasilsesquioxanes have been reported in the literature. The first hexamethylsilsesquioxane (**1.1**) was obtained as a by-product in the synthesis of octamethylsilsesquioxane based on the hydrolytic condensation of methyltriethoxysilane.[3] Subsequently, hexaethylsilsesquioxane has been produced by the hydrolysis of ethyltriethoxysilane. Brown has reported hexacyclohexylsilsesquioxane to be one of the condensation products from the hydrolysis of cyclohexyltrichlorosilane in acetone.[7]

Recently, Feher and co-workers have extended[74] Brown's method of hydrolysis of cyclohexyltrichlorosilane, using acetone/water at room temperature. The reaction mixture was allowed to stand at room temperature for a number of weeks, as shown in Scheme 1.42. Precipitation of $CyT_7(OH)_3$ (**1.29**) occurred after a few weeks.

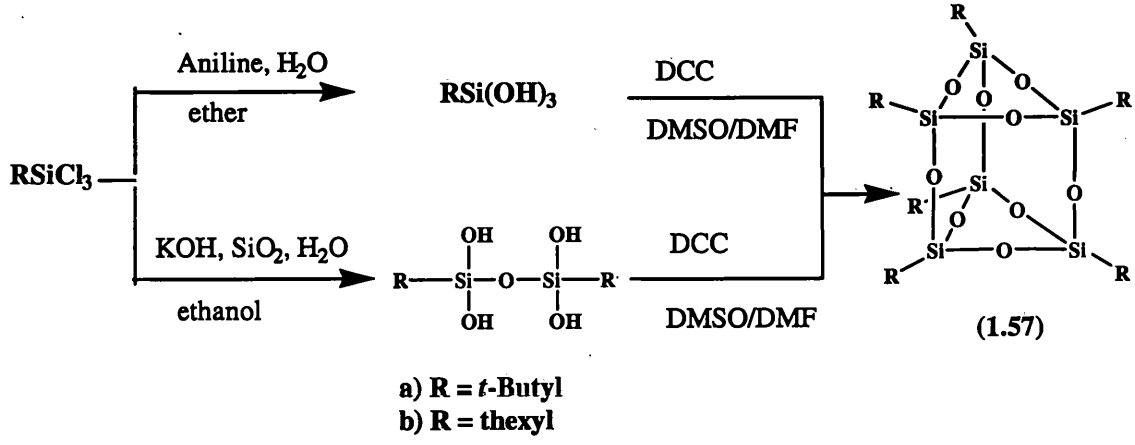


Scheme 1.42

Hexacyclohexylsilsesquioxane **1.55**, CyT_6, was then obtained up until about 12 weeks followed by the partial cages $CyT_7(OH)_3$ **(1.29)** and **1.56**, $CyT_8(OH)_2$.

Molloy and co-workers subsequently modified[75] this method to maximise the proportion of CyT_6, and minimise the yield of $CyT_7(OH)_3$ **(1.29)** in the initial solid product. CyT_6 **(1.55)** was obtained as the main product after 4 months (about 10%). CyT_6 **(1.55)** was characterised by NMR and single crystal X-ray crystallography.

More recently, Unno has described[76] new synthetic routes to produce hexasilsesquioxanes **1.57** in shorter reaction times and higher yields, Scheme 1.43.



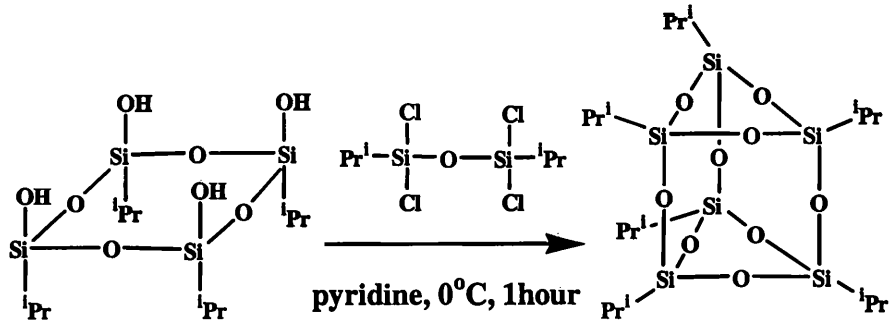
Scheme 1.43

The reactions involved the condensation of silanetriol or tetrahydroxysiloxane using dicyclohexylcarbodiimide (DCC) as the dehydrate reagent. Silanetriol was synthesised by the hydrolysis of $RSiCl_3$ in a mixture of aniline/water/ether. Condensation of thexylsilanetriol with DCC and DMSO involved heating to 120°C for 72 hours to yield 41% of hexathexylsilsesquioxane **1.57a**. Hexathexylsilsesquioxane was fully characterised by NMR and single crystal X-ray crystallography.

Tetrahydroxydisiloxane can be obtained by hydrolysis of $RSiCl_3$ in a mixture of potassium hydroxide/silica/water/ethanol. The condensation of tetrahydroxydi-*t*-butyldisiloxane was

achieved using the same procedure as before, the reaction with DCC in DMSO at 130°C for 72 hours. Hexa-*t*-butylsilsesquioxane **1.57b** was obtained in 25% yield.

Subsequently, Unno[28] has reported the preparation of a hexasilsesquioxane from a tetrahydroxycyclotetrasiloxane (**1.16**) and tetrachlorodi-*iso*-propyldisiloxane, as shown in Scheme 1.44. The reaction was carried out in pyridine, whereby tetrachlorodi-*iso*-propyldisiloxane was added drop-wise to a pyridine solution of tetrahydroxycyclotetrasiloxane (**1.16**) at 0°C and stirred for 1 hour . Hexa-*iso*-propylsilsesquioxane **1.58** was obtained in 25% yield.



(1.58)

Scheme 1.44

1.4 Spherosilicate Cages

Spherosilicate cages are oxygenated derivatives of silsesquioxanes. Since the silicon atoms of spherosilicate cages are connected to four oxygens, it is tetrafunctional and thus called a Q_n. Thus, these compounds will be discussed separately from silsesquioxanes, T_n.

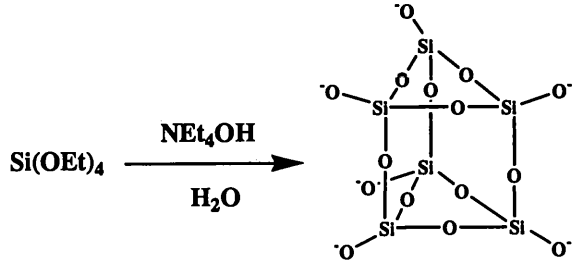
1.4.1 The Hexaspherosilicate cages

The earliest report of a hexaspherosilicate, Q_6R_6, was published by Smolin in 1970.[77] The hexaspherosilicate was synthesised as a nickel salt, $(Si_6O_{15})[Ni(en)_3]_3.26H_2O$, by reacting an ethylenediamine solution of nickel hydroxide with a solution of silica (2.5%) in

ethylenediamine. The product was characterised by single crystal X-ray crystallography. However, the cage structure was shown to be distorted.

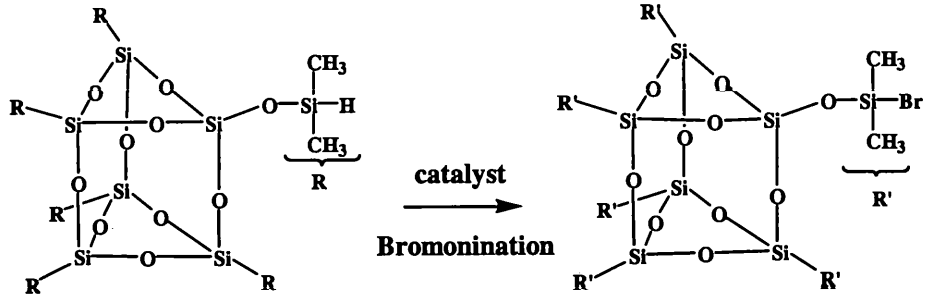
Later, Heobbel and co-workers reported[78] the synthesis of a hexaspherosilicate by reacting silica gel with an aqueous solution of triethylammonium hydroxide for 3 days to give hexatetraethylammonium spherosilicate, $(NEt_4)_6(Si_6O_{15}).57H_2O$. They subsequently described the synthesis of hexatrimethylsilyloxospherosilicate, $(Me_3Si)_6(Si_6O_{15})_6$, by trimethylsilylation of $(NEt_4)_6(Si_6O_{15}).57H_2O$, and its structure was confirmed using single crystal X-ray crystallography.

Recently, Harrison and co-workers have described[79] a new method of obtaining hexaspherosilicates **1.59**, Q_6^-, by the hydrolysis of tetraethoxysilane in an aqueous tetraethylammonium hydroxide solution in a polyethylene bottle, as shown in Scheme 1.45.



(1.59)

Scheme 1.45



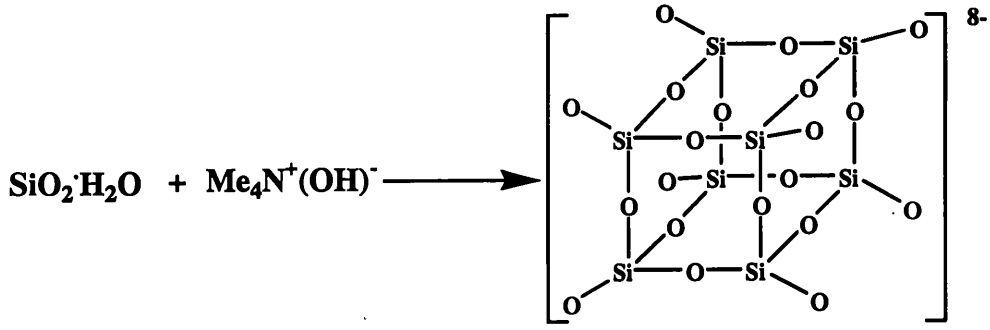
(1.60) **(1.61)**

Scheme 1.46

The Q_6^- was functionalised by reaction with dimethylchlorosilane in a DMF/ heptane mixture to give hexadimethylsilyloxospherosilicate **1.60**, Q_6^H, as a useful precursor to further functionalised silicate cages **1.61**, as shown in Scheme 1.46.

1.4.2 Octaspherosilicate cages

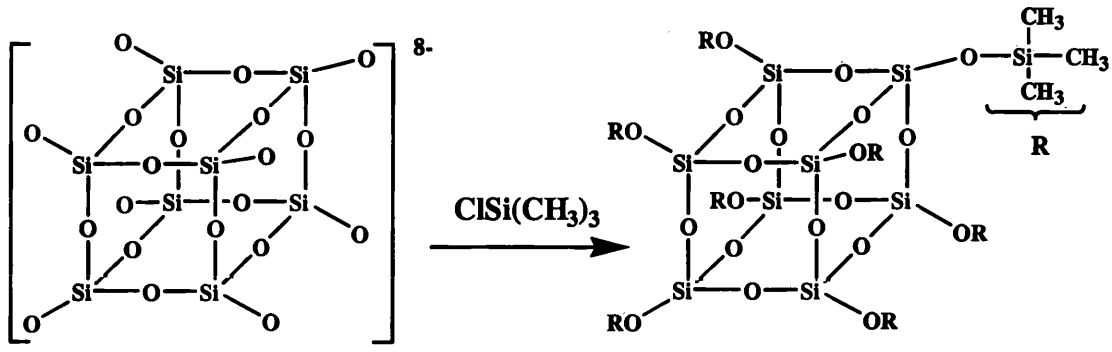
The spherosilicate **1.62**, $(Si_8O_{20})^{8-}$, Q_8^-, was first prepared by Hoebble and co-workers in 1971.[80] The reaction of tetramethylammonium hydroxide solution with silica gel in the ratio of N: Si = 1:1 results in the formation of a crystalline material of composition $[(CH_3)_4N]_8(Si_8O_{20}).69H_2O$, which was shown to contain a cage structure by X-ray crystallography, as shown in Scheme 1.47.



(1.62)

Scheme 1.47

$[(CH_3)_4N]_8(Si_8O_{20})\cdot 69H_2O$ reacts with excess trimethylchlorosilane, $(CH_3)_3SiCl$ to give the trimethylsilyester **1.63**, $(Si_8O_{20})(SiCH_3)_8$, Q_8M_8, in good yield (33%). Functionalised Q_8R_8 cages have also been obtained by silylation of $[(CH_3)_4N]_8(Si_8O_{20}).69H_2O$ with chlorosilanes such as $CH_2=CHSi(CH_3)_2Cl$ and $CH_2=CHCH_2Si(CH_3)_2Cl$, as shown in Scheme 1.48.

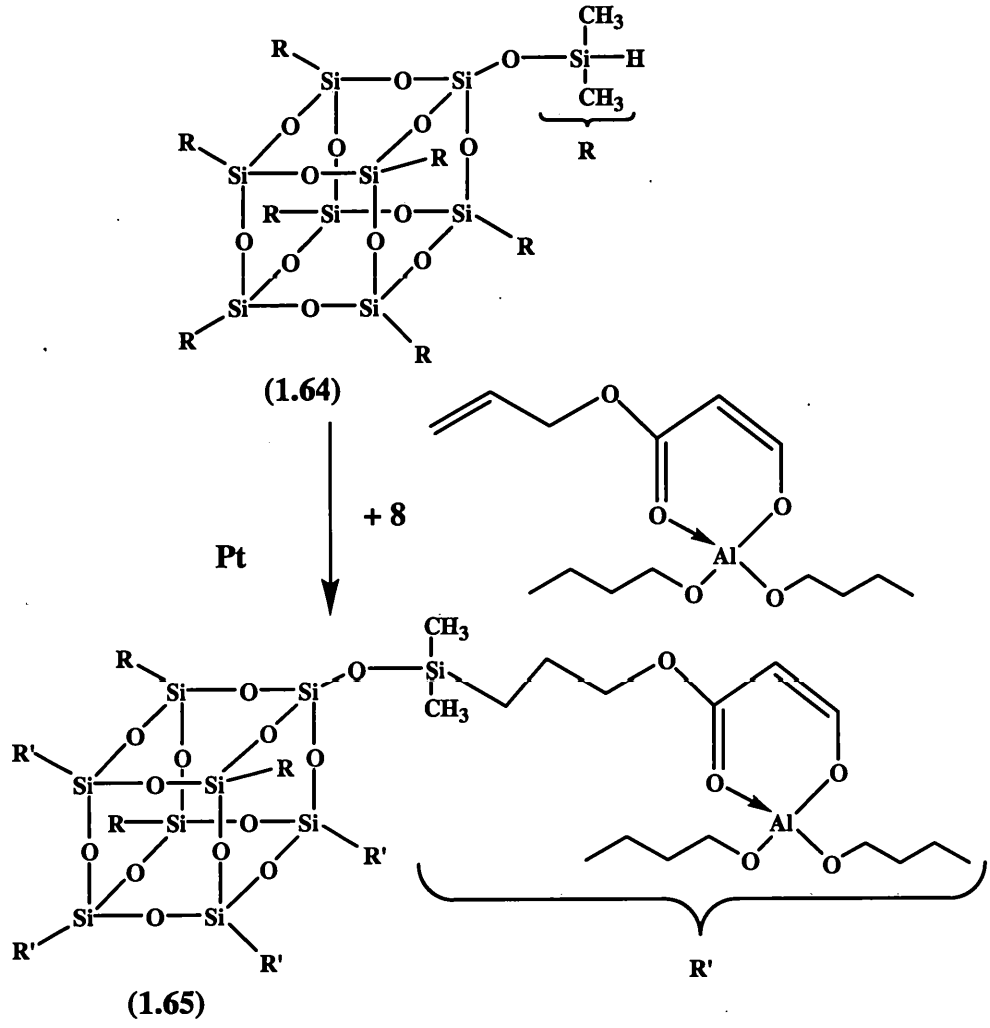


(1.63)

Scheme 1.48

Various methods have been examined to improve the yield of sphereosilicates. Agaskar has developed a facile one-pot route that involves reaction in an immiscible solvent.[81,82]

More recently, Si-H functionalised silicate cages such as spherosilicate cage **1.64** have been prepared that can be hydrosilylated with appropriate alkenes to give a range of new cage **1.65**, as shown in Scheme 1.49.[83] A list of the spherosilicate frameworks that have been prepared is given in Table 1.6.



Scheme 1.49

Table 1.6 Spherosilicate Cages

Framework	Yield (%)	Ref.
$[H(CH_3)_2SiO]_6(SiO_{3/2})_6$	50	79
$[(CH_3)_3SiO]_8(SiO_{3/2})_8$	81	81
$[H(CH_3)_2SiO]_8(SiO_{3/2})_8$	82	27
$[CH_2{=}CH(CH_3)_2SiO]_8(SiO_{3/2})_8$	59	81
$[ClCH_2(CH_3)_2SiO]_8(SiO_{3/2})_8$	47	81

1.5 Applications of Silsesquioxanes

Silsesquioxanes and their homosubstituted derivatives have been used widely in industry. Silsesquioxanes have two unique features. Firstly, the chemical composition ($RSiO_{3/2}$), is intermediate between that of silica (SiO_2) and silicones $(R_2SiO)_n$. Secondly silsesquioxane molecules are physically large – on a part with polymer dimensions. Thus silsesquioxanes have been widely used in industry as copolymers,[84] additives of plastics[85] and preceramics etc..

Polysilsesquioxanes have an important role in polymer chemistry.[86] In particular, ladder-like silsesquioxanes have found use as electrical insulators for large-scale integrated circuits.[87,88] Thin film polysilsesquioxanes,[89,90] $(RSiO_{3/2})_8$, R = H, CH_3, C_6H_5, have been used as low dielectric insulators for applications in microelectronics.

1.6 Mechanism of Formation of Silsesquioxanes

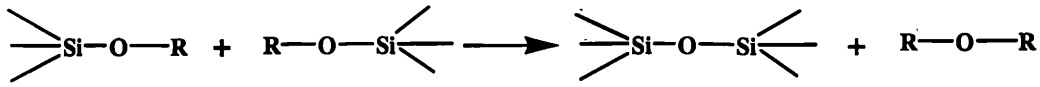
1.6.1 Hydrolytic Polycondensation of $RSiX_3$

$$nRSiX_3 + 1.5nH_2O \longrightarrow (RSiO_{3/2})_n + 3nHX$$

Scheme 1.50

Scheme 1.50 summarises the formation of silsesquioxanes in the hydrolytic condensation of trifunctional monomer, $RSiX_3$, in diluted solvents. Despite its apparent simplicity this involves a multiple-step and rather complicated process. The formation of the individual Si-O-Si units that lead to silsesquioxanes can arise from homofunctional condensation or heterofunctional condensation as shown in Scheme 1.51, Scheme 1.52 and Scheme 1.53.

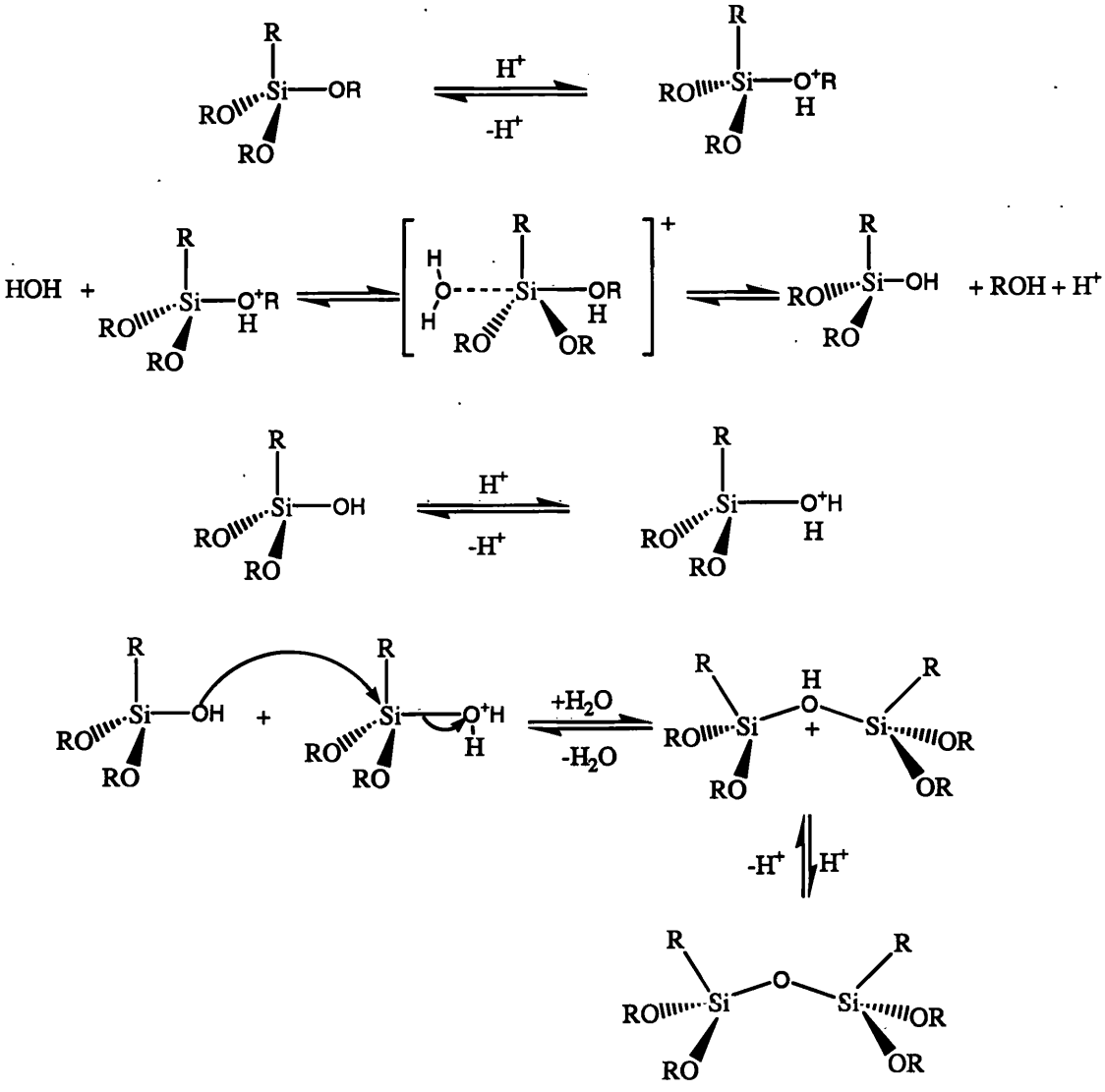
Scheme 1.54 gives a more detailed picture of the condensation and hydrolysis equilibrium involved in the dimerisation of silanols, and shows just how complex the mechanisms are.[83]



Scheme 1.51

Scheme 1.52

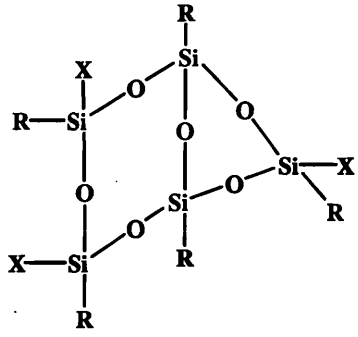
Scheme 1.53



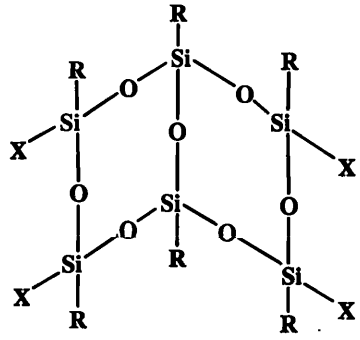
Scheme 1.54

Previous work on the mechanism of hydrolytic condensation of trihalosilanes to give silsesquioxane cages has been mainly based on the identification of intermediates that have been isolated. In general, different analytical techniques have been used for identification of intermediates and products of hydrolytic condensation, such as FT-IR, NMR (solution and solid state), GC, HPLC (SEC and GPC), GC-MS and mass spectrometry (EI, FAB, MALDI-TOF). While GC-MS[91] is significantly useful for volatile silsesquioxanes, NMR[92-94,95-97] and MALDI-TOF[98-101] are the most promising diagnostic techniques for characterisation of most silsesquioxanes.

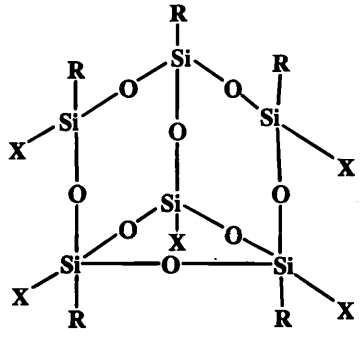
Among the intermediates of trichlorosilanes, $RSiCl_3$, polycondensation, linear silsesquioxanes containing two to four silicon atoms, cyclosiloxanes, $(RXSiO)_n$ with n = 3-7 and R = OH, OR, and condensed polycyclosiloxanes **1.66-1.71**, have been isolated.[21,91]



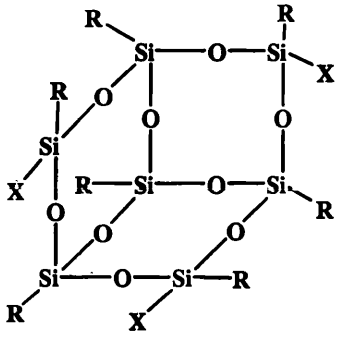
(1.66)



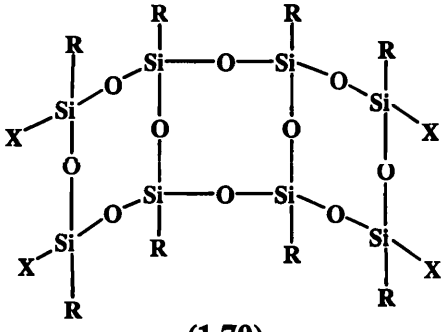
(1.67)



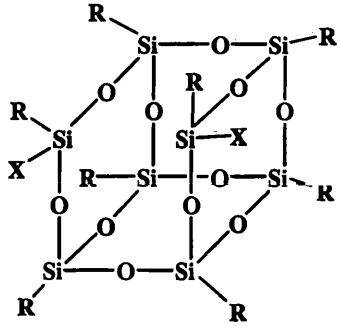
(1.68)



(1.69)

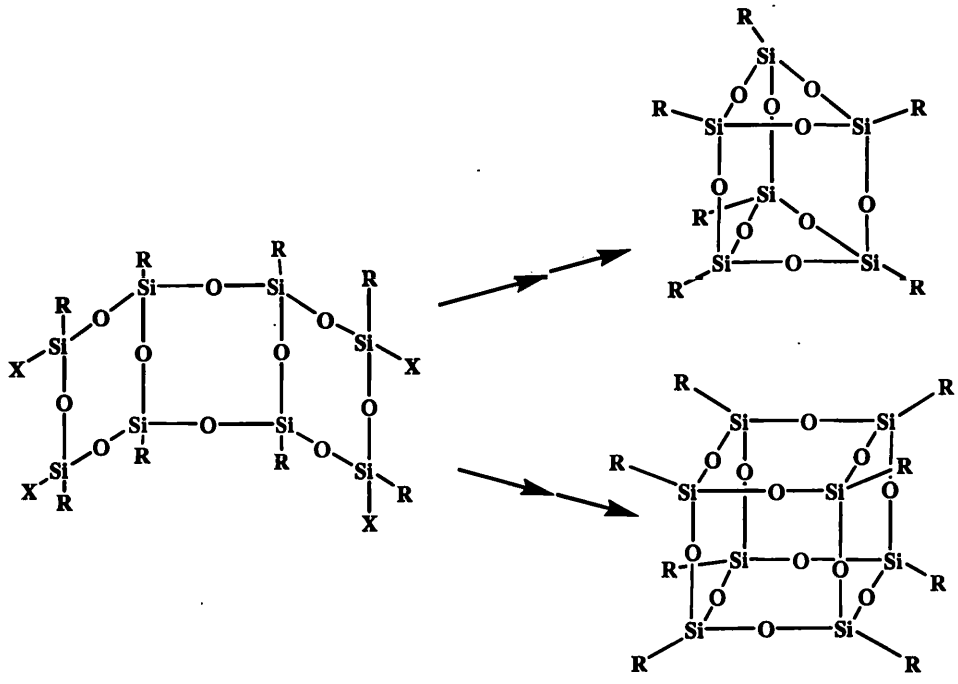


(1.70)



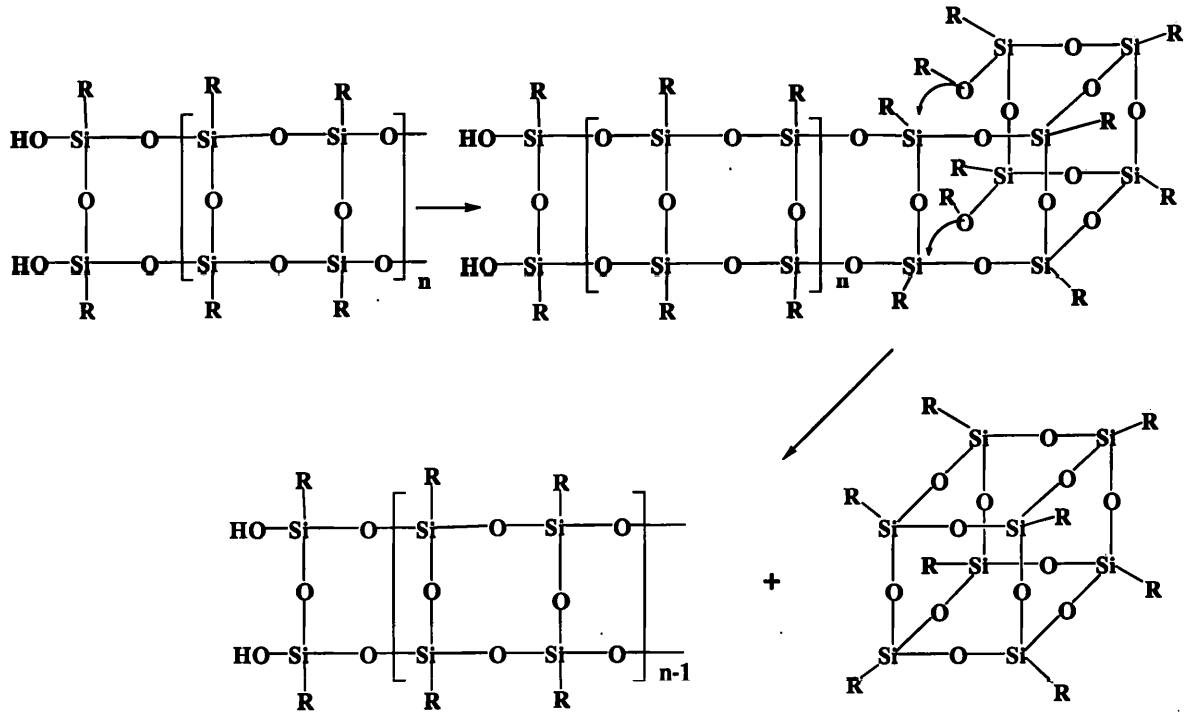
(1.71)

The structure and yield of the various intermediates depends heavily on the reaction conditions and the reactivity of the initial monomers. Sprung and Guenther[2,3,19] were the first to suggest that the hydrolysis of organyltrifunctional monomer, $RSi(OR')_3$, involves the formation of linear, cyclic, polycyclic and finally, polyhedral siloxanes, consecutively, and assumed the chain growth to be of a random nature, Scheme 1.55.

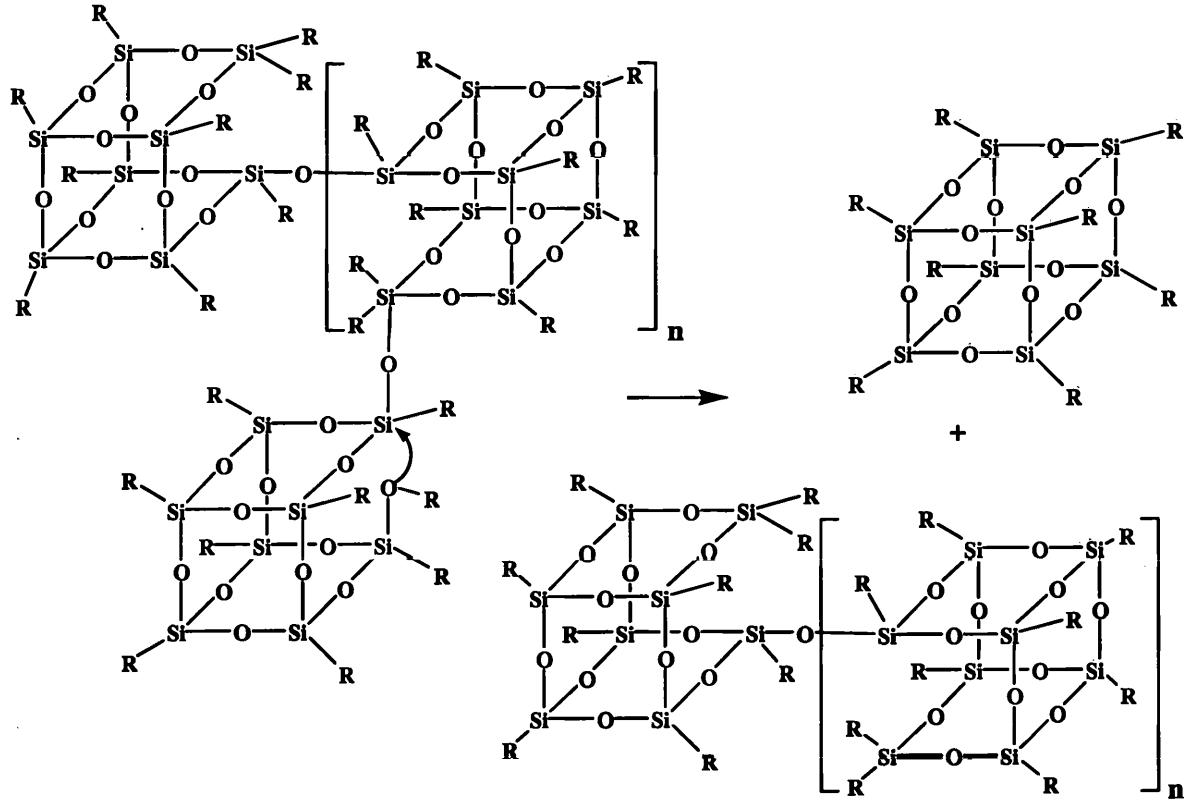


Scheme 1.55

The mechanism of condensation of phenyltriethoxysilane, $PhSi(OEt)_3$, at high temperature was suggested[19] to involve a nucleophilic interaction of the terminal silanol groups with neighbouring siloxane bonds. Two possible polymer structures were suggested as precursors for the octaphenylsilsesequioxanes, PhT_8, ladder-like polymers and linear block structures. In the presence of alcoholic alkali, condensation at high temperature produces a large number of incompletely condensed low molecular weight oligosiloxanes containing one or more alkoxy groups. When the cyclotetrasiloxane rings of the polymers have a *cis-syn-cis* arrangement, octasilsesquioxanes, T_8R_8 can be formed as shown in Scheme 1.56 and Scheme 1.57

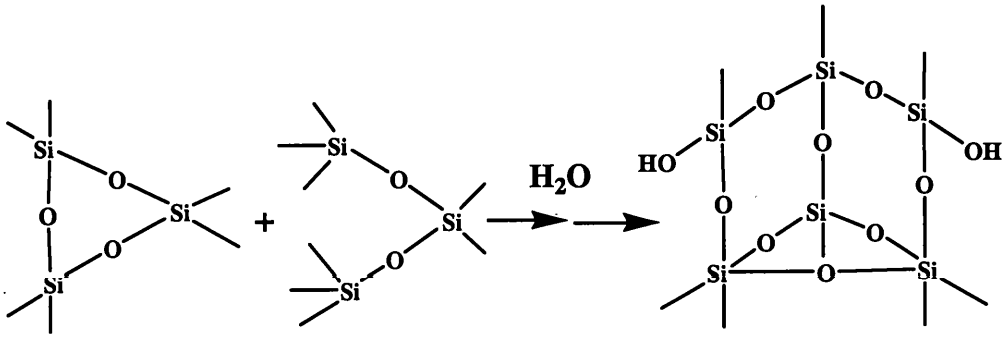


Scheme 1.56

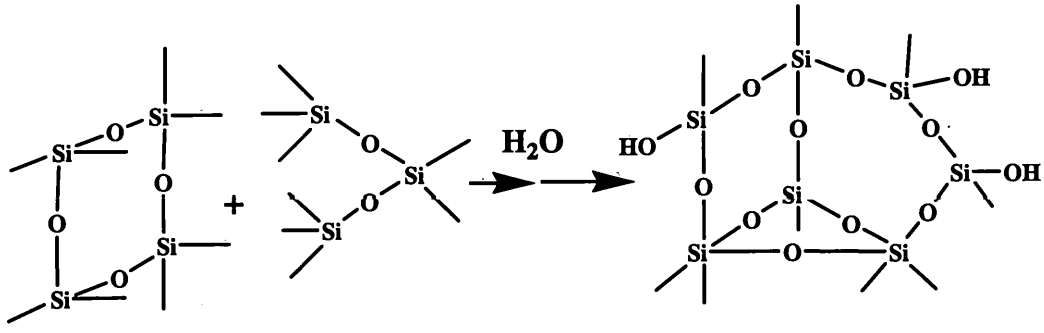


Scheme 1.57

This hypothesis was further developed by Brown and co-workers,[5] who studied the hydrolysis of cyclohexytrichlorosilane and phenyltrichlorosilane. They suggested that the formation of polyhedral silsesquioxanes and their homoderivatives, occurred as a result of consecutive stepwise polycondensation of cyclic macromolecules, as shown in Scheme 1.58 and Scheme 1.59, respectively.[7]

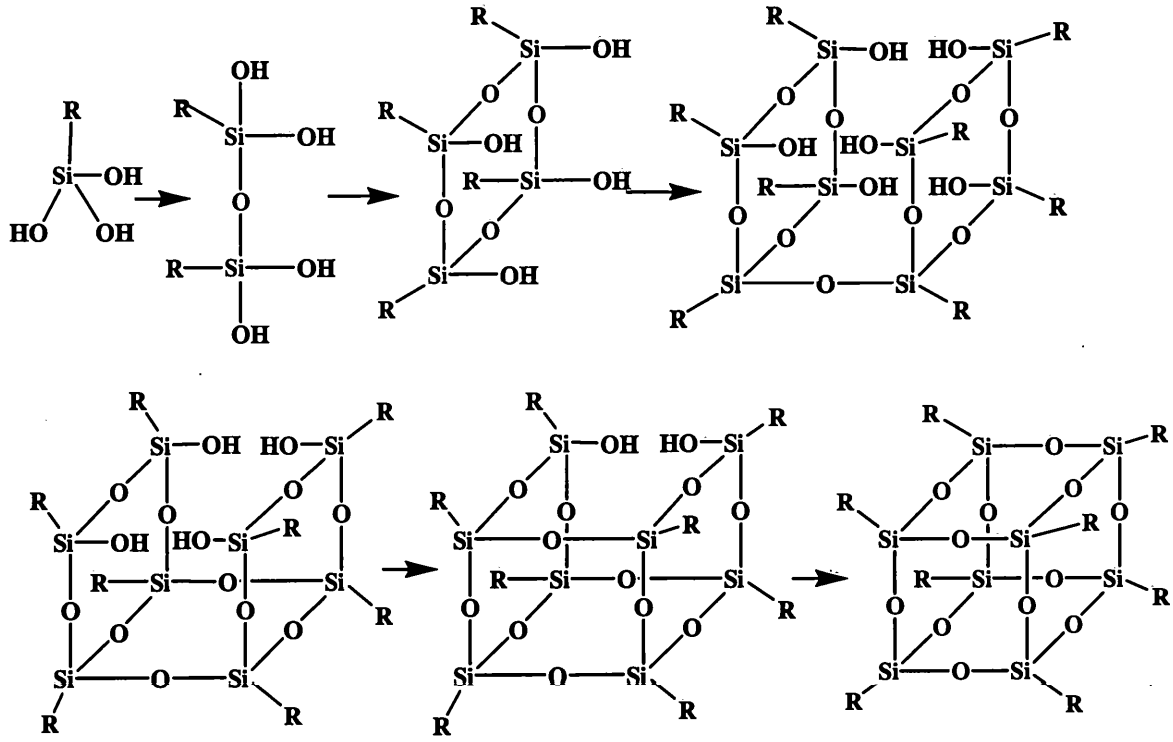


Scheme 1.58

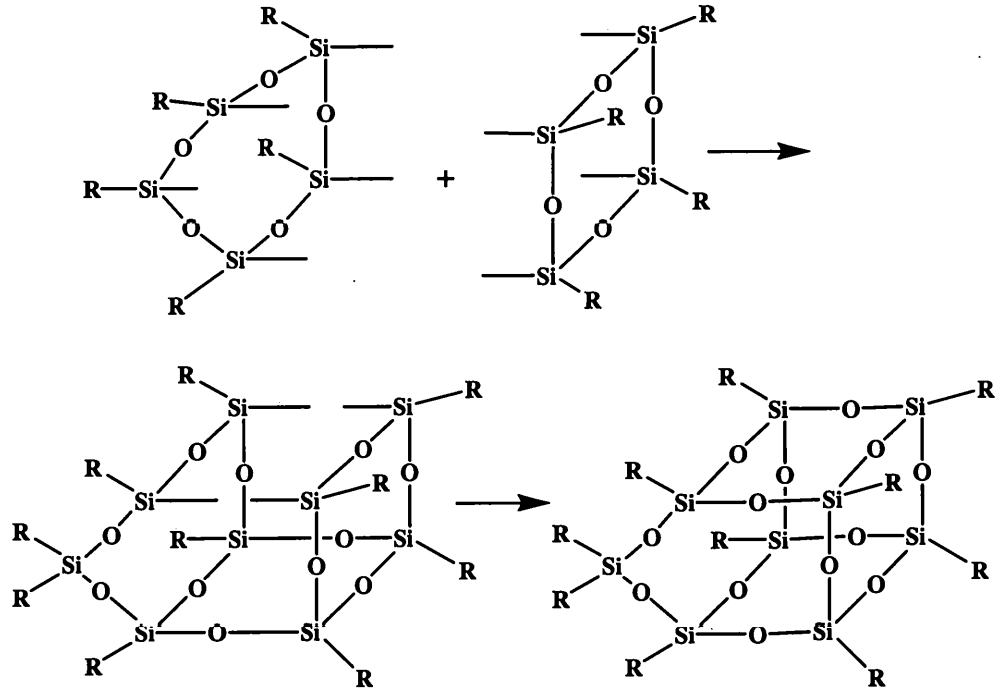


Scheme 1.59

On the basis of the polycondensation intermediates identified in the mixture, the initial steps of the reaction were thought to involve simultaneous formation of linear and cyclic oligosiloxanes. Co-condensation of the latter was believed to lead to polycyclosiloxanes. Since octasilsesquioxane is a relatively stable species it does not undergo further rearrangement or intermolecular polycondensation, Scheme 1.60 and Scheme 1.61.[7]



Scheme 1.60



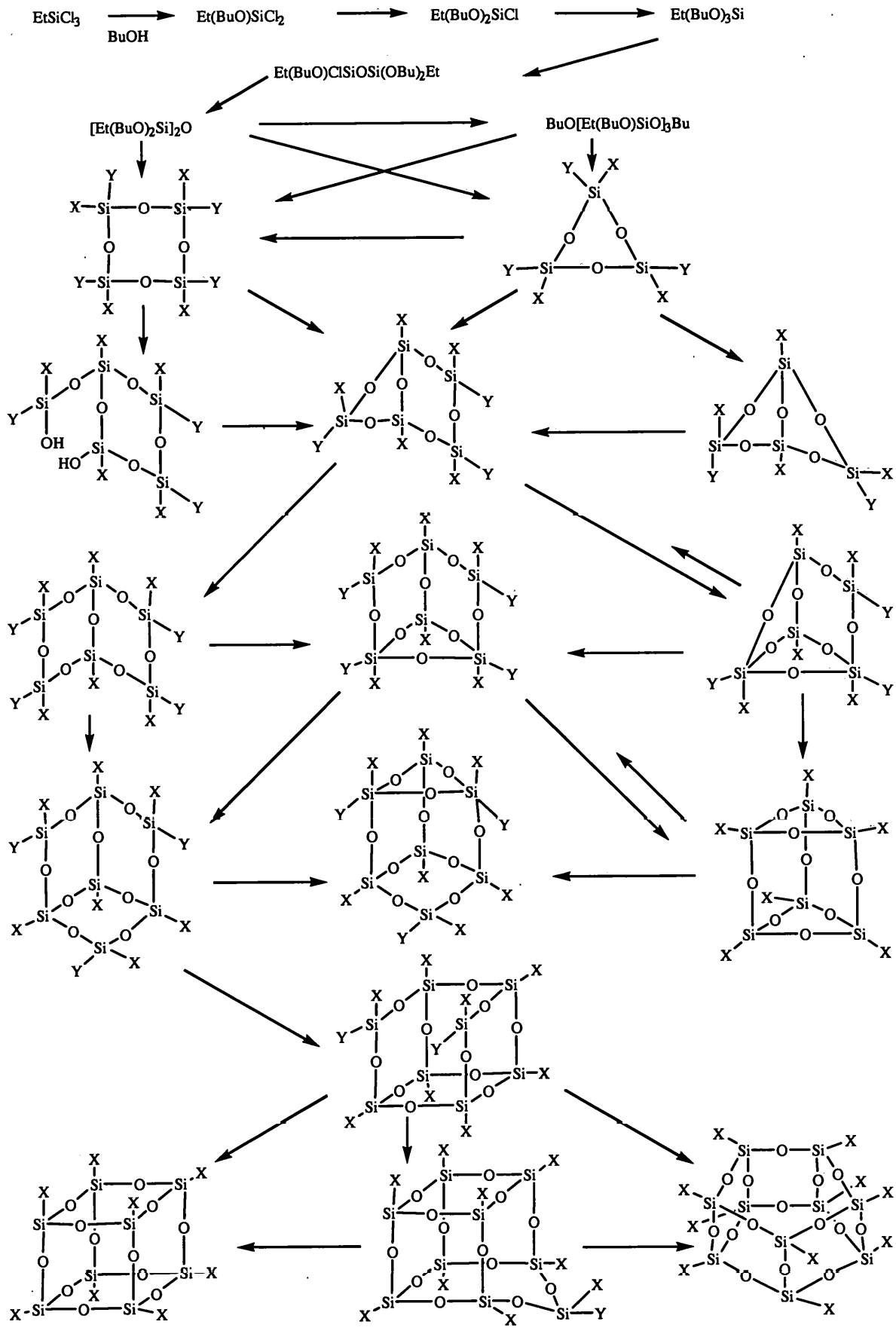
Scheme 1.61

Different substituents of triethoxysilane, $RSi(OEt)_3$, would lead to different silsesquioxane cages. This can be explained by structural differences in the functional groups. For example, the silanol groups in the various phenylpolycyclosiloxane intermediates, would

have differing reactivity due to the accessibility of the OH groups in the different structures and their availability for hydrogen bonding.

By studying the hydrolysis of cyclohexyltrichlorosilane and phenyltrichlorosilane, Brown speculated that the resulting silsesquioxanes were formed by different mechanisms, depending on the end products of polycondensation. Cyclohexyltrichlorosilane gives mainly CyT_6 cages and $CyT_7(OH)_3$, whereas under the same conditions, hydrolysis of phenyltrichlorosilane affords oligomer and polysiloxanes of higher molecular weight.

The mechanism by which ethylsilsesquioxanes was formed by the hydrolysis of ethyltrichlorosilane and ethyldichlorosilane in butanol has been established by GC-MS, as shown in Scheme 1.62.[9] All the products formed were identified by GC-MS.


EtSiCl3
BuOH
Et(BuO)SiCl2
Et(BuO)2SiCl
Et(BuO)3Si
Et(BuO)ClSiOSi(OBu)2Et
[Et(BuO)2Si]2O
BuO[Et(BuO)SiO]3Bu

Scheme 1.62

1.6.2 Condensation of Si-functionalised cyclosiloxanes, $(RXSiO_{2/2})_n$

The mechanism of formation of silsesquioxanes by hydrolytic condensation of cyclosiloxanes, $(RXSiO)_n$, is probably similar to the latter steps of the hydrolytic polycondensation of etheyltrichlorosilane and involves cleavage of Si-H, Si-OH and Si-OR bonds, together with Si-O-Si groups. This condensation has been studied for $C_2H_5Si(OH)_4$. The higher yield of polyhedral oligoethylsilsesquioxanes and their homo derivatives as well as that of the intermediate tricyclosiloxanes, suggest the Brown-Vogt mechanism shown in Scheme 1.60 and Scheme 1.61, in which oligosilsesquioxanes result from a stepwise polycondensation of cyclic macromolecules.

1.6.3 Hydrosilylation of silsesquioxanes

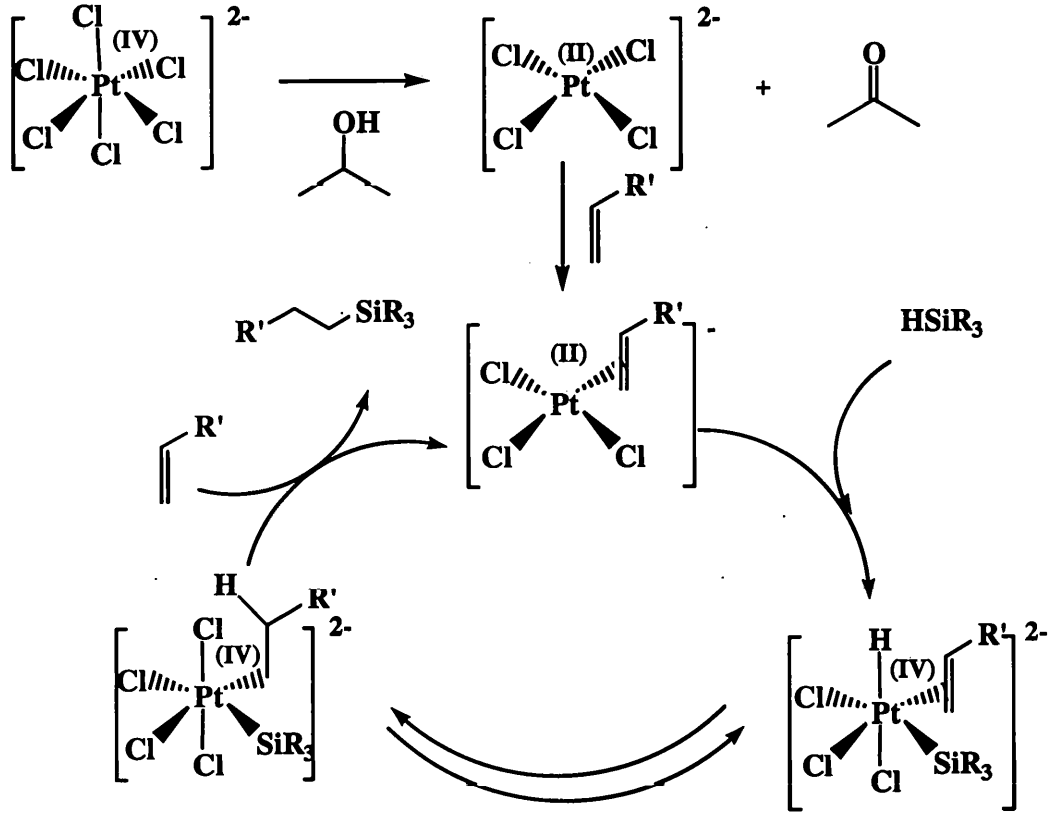
The mechanism of hydrosilylation of 1-octene with trichlorosilane was first described[102] in 1947, as a free radical reaction. Based on this mechanism, a number of refinements and developments were subsequently achieved. More recently, the reaction was found to be catalysed by transition metals such as platinum. Among the many catalysts employed, Speier's catalyst, hexachloroplatinic acid, H_2PtCl_6, in *iso*-propan-2-ol, is the one most frequently quoted. The reaction mechanism of this catalytic hydrosilylation was first proposed by Chalk and Harrod,[103] as shown in Scheme 1.63. Pt^{IV} is first reduced to Pt^{II} by *iso*-propanol. Ligand exchange of the Cl^- by $R'CH{=}CH_2$ gives a Pt^{II} complex, which undergoes oxidative addition of R_3SiH to give a Pt^{IV} complex (a π to σ change). Reductive *syn* elimination completes the reaction cycle.

In the 1980's Lewis and co-workers[104,105] proposed an alternative mechanism involving a Pt^0 species as the catalyst, whereas Chalk and Harrod employed H_2PtCl_6. However, the outcomes of the two mechanisms were the same, although Lewis and co-workers reported that the catalytically active species was in fact colloidal particles of platinum.

Many other transition metal complexes can be employed as catalysts in hydrosilylation reactions, such as rhodium catalysts[106] and nickel catalysts[107] etc..

In general, hydrosilylation reactions are accompanied by a series of side reactions that reduce the yield of the desired products. The main side reactions are:

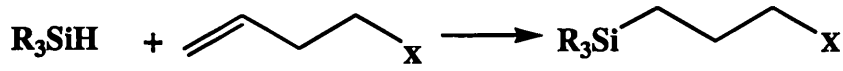
1. α and β addition of the silane to the alkene
2. Isomerisation of the alkene
3. Reaction of the silane with protic species
4. Disproportionation of the hydrosilane
5. Metal-catalysed Si-C bond cleavage



Scheme 1.63

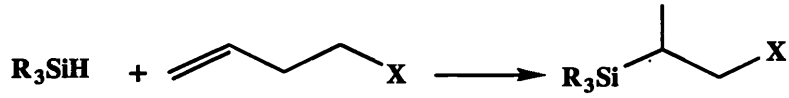
The addition of the silane across the alkene can occur in both the Markownikov and anti-Markownikov sense.

a) β- or anti-Markownikov addition



Scheme 1.64

b) α- or Markownikov addition



Scheme 1.65

α and β addition has been found to depend upon the catalyst used and the reactivity of the R group of the R_3SiH.

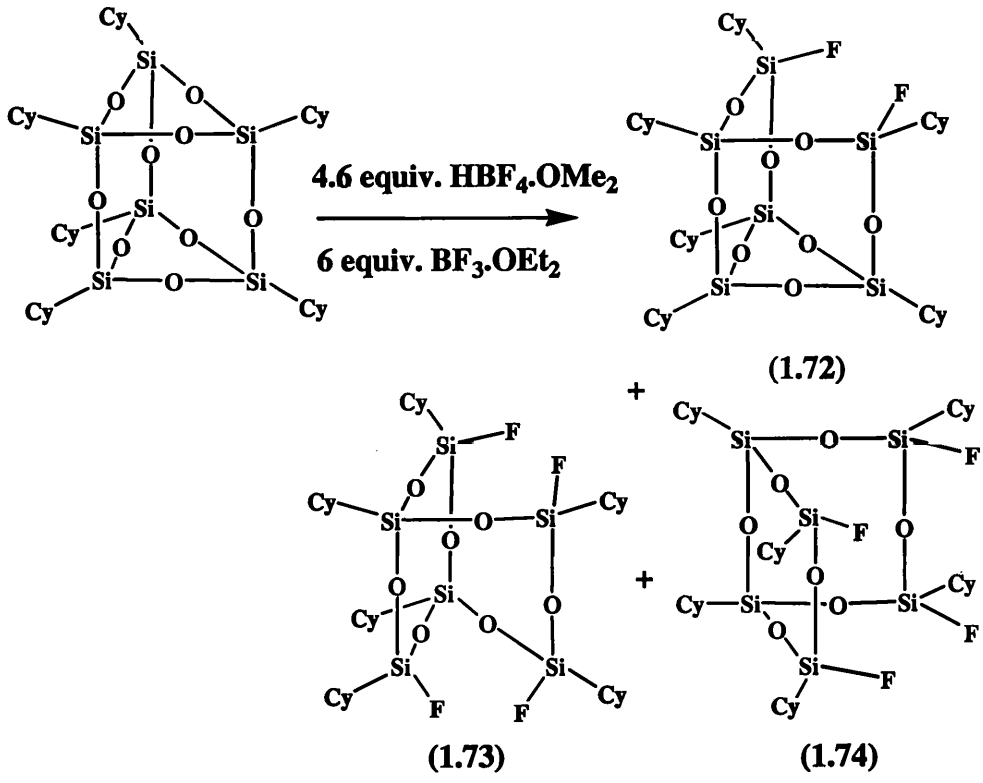
In summary, although the mechanism of synthesis of silsesquioxane cages by hydrosilylation is very clearly explained with both Markownikov and anti-Markownikov addition, the mechanism of synthesis of silsesquioxane cages from trifunctional monomers, $RSiX_3$ and from Si-functionalised cyclosiloxanes, $(RXSiO_{3/2})_n$, is still not fully understood. Thus the investigation of the formation of the silsesquioxane cages remains an interesting area.

1.7 Degradation and Rearrangement of Silsesquioxane Cages

Investigations of the degradation and rearrangement of silsesquioxane cages have focussed on the treatment of silsesquioxanes with a variety of nucleophiles and electrophiles.

Fully condensed silsesquioxanes cages have been cleaved to give partial Si-O-Si frameworks under acid or basic conditions.

Degradation of silsesquioxane cages has been recently studied by Feher and co-workers.[108,109] Treatment of hexacyclohexylsilsesquioxane, CyT_6, with a strong organic acid, a mixture of HBF_4/BF_3 in organic solvents, cleaved two of the Si_3O_3 rings to give an F-Si-O framework, without initiating the formation of T-gel, Scheme 1.66. The reaction of CyT_6 with HBF_4/BF_3 in deuterium chloroform was very rapid, such that the reaction products could be followed by ^{13}C, ^{29}Si, and ^{19}F NMR spectroscopy. .

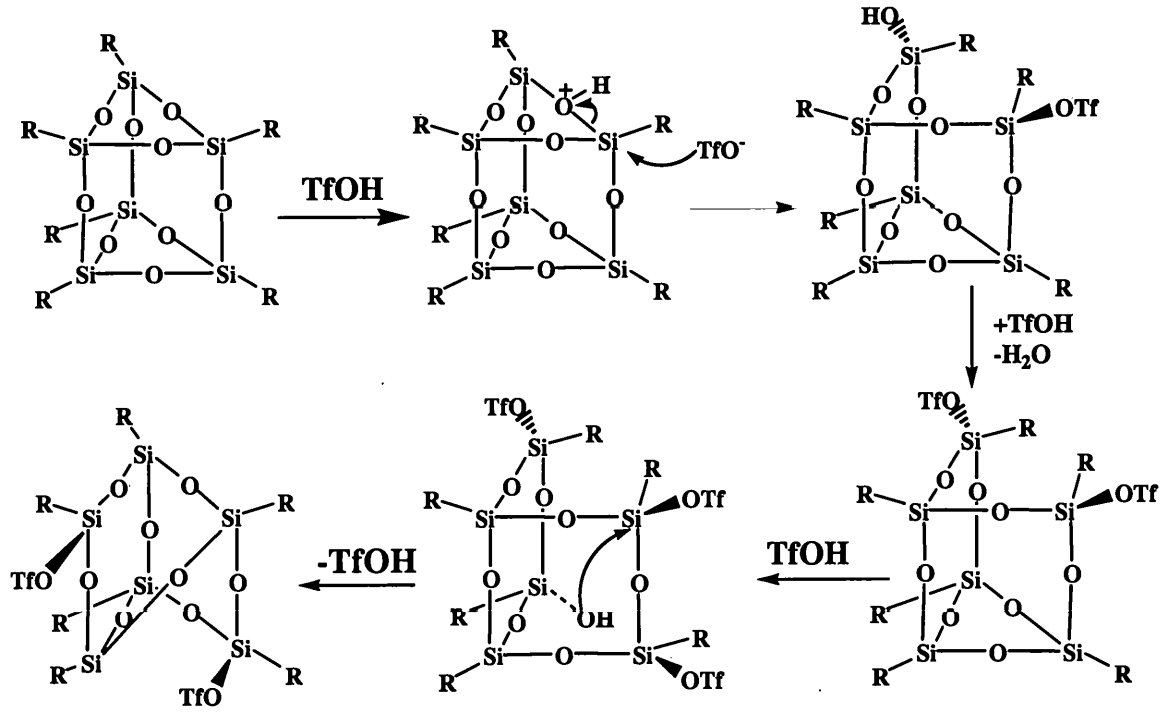


Scheme 1.66

When using 1.5 equivalents of $HBF_4.OMe_2$ and 2.3 equivalents of $BF_3.OEt_2$, the major product observed by NMR, is the difluoride **1.72** (68%) with some unreacted starting material CyT_6 (8%), as well as a small amount of tetrafluoride **1.73** (14%) and **1.74** (<1%). When 4.5 equivalents of $HBF_4.OMe_2$ and 7 equivalents of $BF_3.OEt_2$ were used all of the

starting material CyT_6 was consumed to produce a mixture of **1.72** (32%), **1.73** (56%) and **1.74** (13%). When excess $HBF_4{\cdot}OMe_2$ and $BF_3{\cdot}OEt_2$ was employed, the only products observed were tetrafluoride **1.73** and **1.74**. The observation that all the starting material, CyT_6, was consumed to produce products such as **1.72** indicates that CyT_6 was significantly more susceptible to cleavage by HBF_4/BF_3 than the difluoride **1.72** and this difluoride **1.72** was a relatively stable product and a logical precursor to **1.73** and **1.74**.

A similar cleavage reaction of CyT_6 was observed with triflic acid, CF_3SO_3H, (TfOH), and other strong acids.[110] CyT_6 was treated with TfOH, and the Si_3O_3 rings were observed to be cleaved in preference to the Si_4O_4 rings. This was coupled with selective Si_4O_4 ring formation and conversion of the Si-OH groups into Si-OTf, compound **1.75**. The reaction mechanism that was proposed is shown in Scheme 1.67.

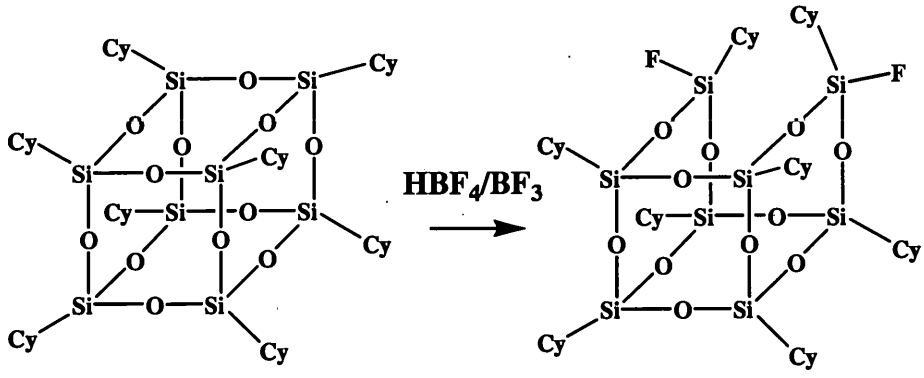


(1.75)

Scheme 1.67

The release of ring strain in the Si-O framework is clearly an important driving force in this process. The water formed during the reaction does not react with ditriflate **1.75** because of protonation by the strong acid. Most of the nucleophilic substitution reactions of the triflate-substituted silsesquioxanes were observed to take place with complete inversion of stereochemistry at the silicon atom.

Feher and co-workers have reported[109] that one Si-O-Si linkage of octasilsesquioxane could be cleaved to form a partial framework using strong acids, such as HBF_3/BF_4 and TfOH. Octacyclohexylsilsesquioxane, CyT_8, was treated with a mixture of 4.6 equivalents of $HBF_4.OMe_2$ and 6 equivalents of $BF_3.OEt_2$, and a difluoride **1.76** was isolated (70-80%), as shown in Scheme 1.68. Water is produced in this reaction which lowers the activity of HBF_4 to such an extent that protonation and subsequent cleavage of Si-O-Si linkages is no longer favourable.

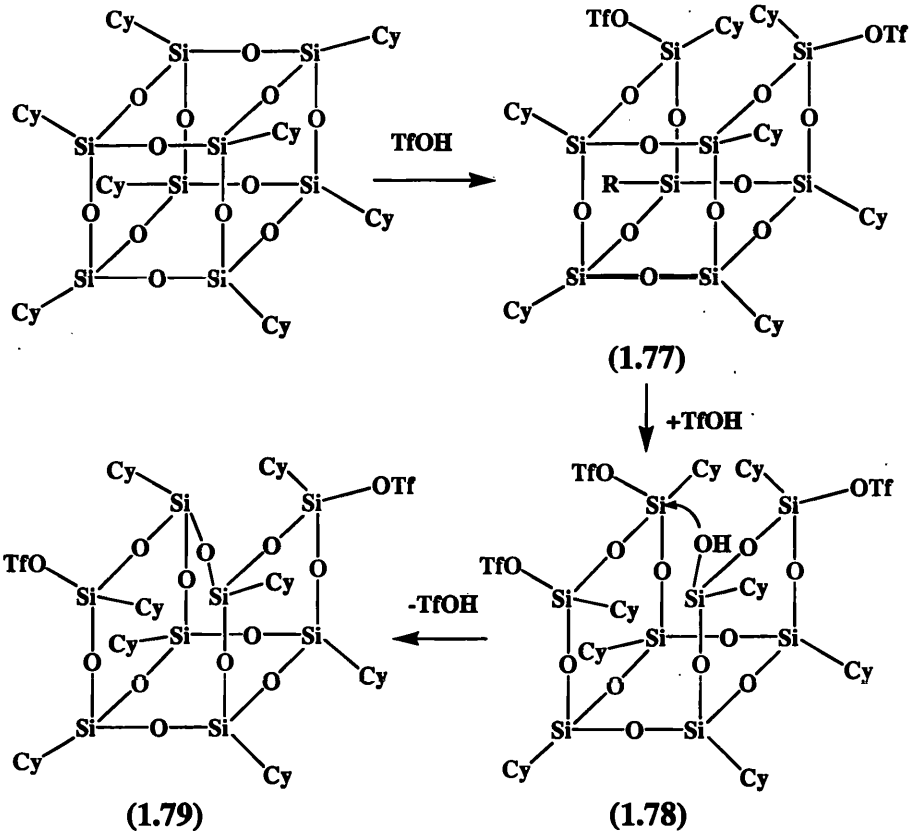


(1.76)

Scheme 1.68

Whilst one Si-O-Si linkage of CyT_8 cage could be cleaved to form a ditriflate **1.77** when 5 equivalents of TfOH were employed, reaction of CyT_8 with a large excess of TfOH (10 equivalents), cleaved additional Si-O-Si linkages. However, the major product was not the expected tetratriflate **1.78**, which would be derived from simple cleavage of a second Si-O-Si linkage.

A new symmetric framework **1.79** was obtained in high yield (70%), which still contained only two Si-OTf groups. The proposed mechanism for its formation is shown in Scheme 1.69. Complete inversion of stereochemistry at the silicon atoms is observed in each cleavage of the Si-O-Si linkage and intramolecular displacement of the triflate groups, as shown in Scheme 1.69.

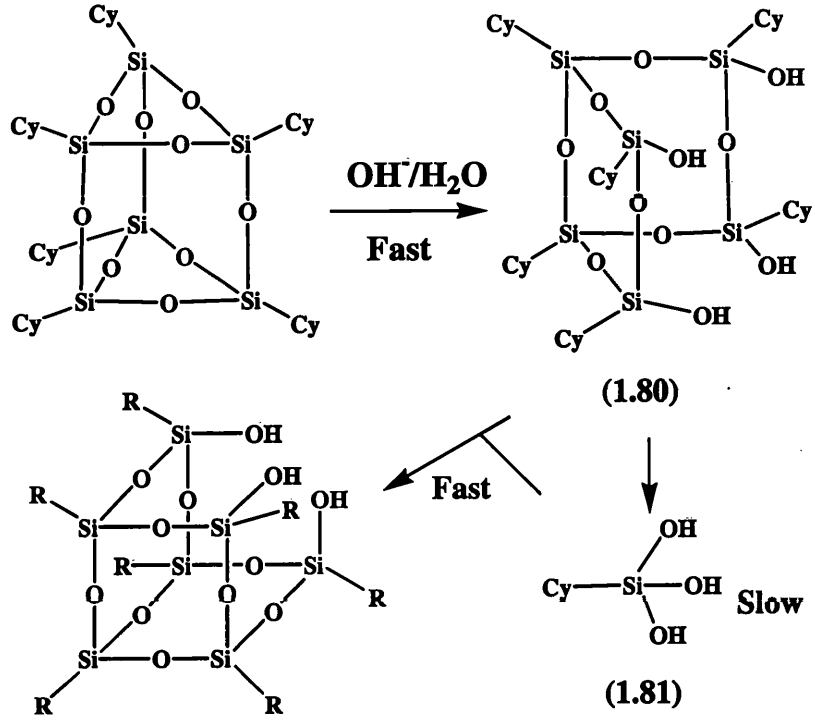


Scheme 1.69

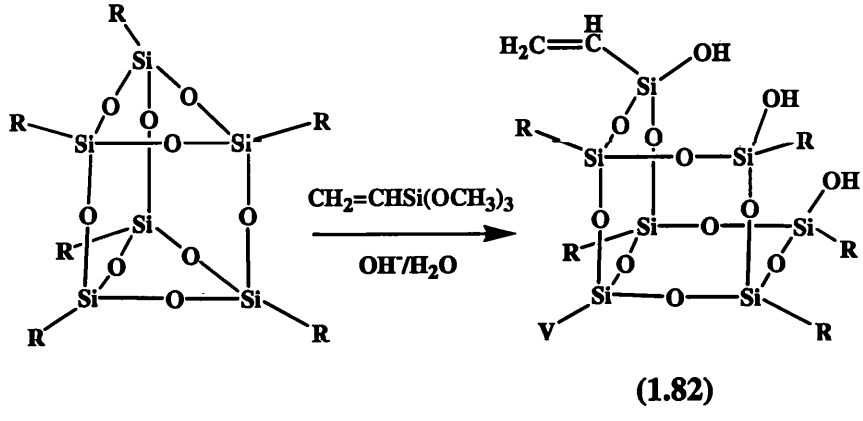
Under basic conditions, both Si_3O_3 rings of the hexacyclohexylsilsesquioxanes, CyT_6, undergo ring opening to give the tetrol **1.80**. The triol silsesquioxane, $CyT_7(OH)_3$ was then formed at the expense of the tetrol **(1.80)**, as shown on Scheme 1.70.

Reaction of CyT_6 with aqueous tetraethylammonium hydroxide in THF occurred rapidly over a period of several hours at room temperature.[111] A first product was isolated in 63% yield after one hour. ^{29}Si NMR showed this product to be the tetrol **(1.80)**, which exhibited

two resonances at δ -59.4 and -68.8 ppm with a relative integration of 4:2. The triol, $CyT_7(OH)_3$, was obtained if the reaction was allowed to continue for several hours. These results suggest the mechanism shown in Scheme 1.70, which highlights the formation of a highly reactive species **1.81** and reacts with the tetrol **(1.80)** incorporating a one silicon unit to form the $CyT_7(OH)_3$, This is followed by further cleavage to give the monomer **1.81.**



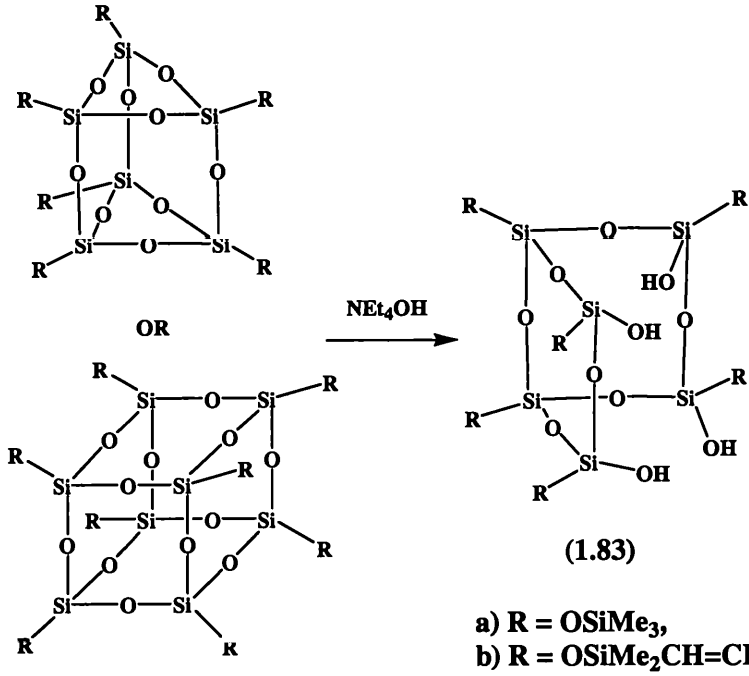
Scheme 1.70



Scheme 1. 71

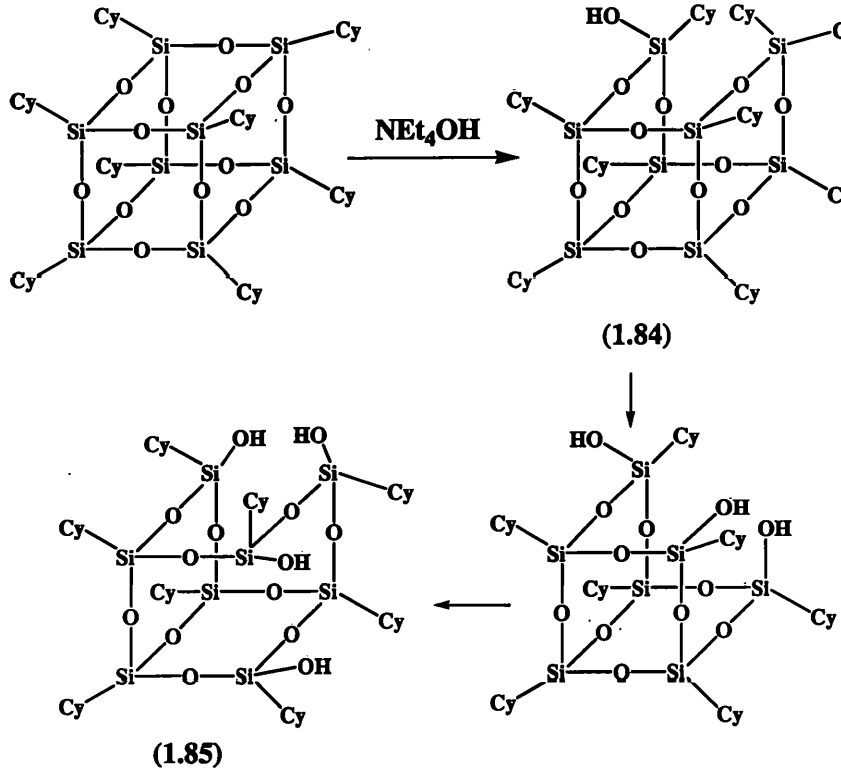
This hypothesis was confirmed by the reaction of CyT_6 with aqueous tetraethylammonium hydroxide in the presence of vinyltrimethoxysilane, which afforded the trisilanol **1.82**, as shown in Scheme 1.71.

The reaction of Q_6R_6 with tetraethylammonium hydroxide occurred very rapidly at low temperature (-40 to -25°C), to produce a new silicate cluster, the tetrol **1.83**.[112]



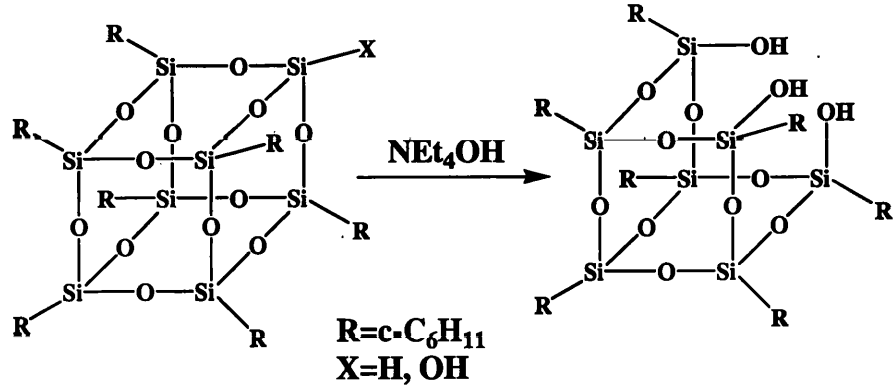
Scheme 1.72

Tetraethylammonium hydroxide was also used for the degradation and rearrangement of homo and heterosilsesquioxane cages. The reaction of octacyclohexylsilsesquioxane, CyT_8, with aqueous tetraethylammonium hydroxide in THF proceeded in one hour at room temperature to give a diol **1.84** in 80% yield, as shown in Scheme 1.73.[113] The alternative framework, $CyT_7(OH)_3$, was obtained with another product, a tetrol **1.85**, when the reaction was left for a longer time. After 9 hours, the ratio of starting material CyT_8:**1.84**:**1.85**:$CyT_7(OH)$ is 6:18:26:50.



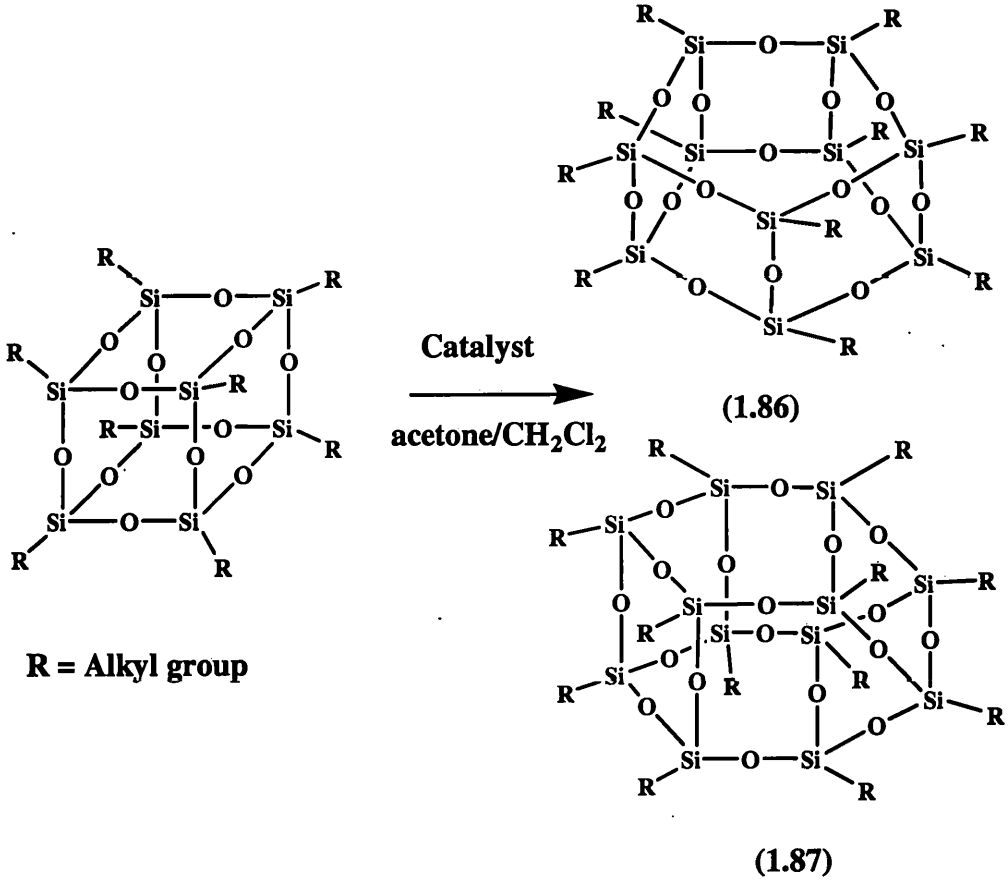
Scheme 1.73

The hetereosilsesquioxane framework $R'R_7(SiO_{3/2})_8$ reacted similarly with tetraethylammonium hydroxide to give analogous products in good yield (>50%). The results clearly demonstrated that silicon centres possessing an H or OH group were much more readily eliminated from the CyT_8 framework than a silicon centre that possessed relatively bulky, Cy groups.



Scheme 1.74

Marsmann and co-workers have recently reported[114] that T_8R_8 cages can be rearranged to higher molecular weight silsesquioxane cages, decasilsesquioxanes **1.86**, $T_{10}R_{10}$ and dodecasilsesquioxane **1.87**, $T_{12}R_{12}$, using strong bases, as shown in Scheme 1.75. Table 1.7 lists the data of Marsmann and co-workers on the redistribution of T_8R_8 to $T_{10}R_{10}$ and $T_{12}R_{12}$.



Scheme 1.75

However, Marsmann and co-workers did not report all of the experimental details or the reaction mechanism by which the T_8R_8 cages were rearranged.

In summary, the degradation and rearrangement of T_6R_6 and T_8R_8 cages have been reported. However, only three types of catalysts have been used, HBF_4/BF_3, triflic acid tetraethylammonium hydroxide and a few nucleophilic bases. Thus, there is still the potential for the investigation of other catalysts, which may cause the cage degradation.

Table 1.7 Rearrangement of T_8R_8 from Marsmann and co-workers

R=	% $R_8(SiO_{3/2})_8$	% $R_{10}(SiO_{3/2})_{10}$	% $R_{12}(SiO_{3/2})_{12}$	Catalyst
		Solvent: acetone		
C_2H_5	41	55	4	A
C_3H_7	88	12		A, B
ClC_3H_6	23	60	17	C, D, E, F
BrC_3H_6	64	36		C, D, E
IC_3H_6	88	12	26	B, C
$NCSC_3H_6$	18	56		C, D, E, F
$C_6F_5C_3H_6$	51	49		D, E, F
C_4H_9	82	18		A
C_5H_{11}	90	10		A
C_7H_{15}	96	4		A
C_8H_{17}	85	15		A
C_9H_{19}	92	8		A
$C_{10}H_{21}$	93	7		A
		Solvent: acetonitrile		
ClC_3H_6	28	61	11	G, H, I
BrC_3H_6	93	7		I
IC_3H_6	97	3		I
$NCSC_3H_6$	18	62	20	G, H, I
$C_6F_5C_3H_6$	48	52		G, H

A: K_2CO_3, B: NaOH, C: NaOCN, D: CH_3COONa, E: NaOH, F: Na_2SO_3,

G: Na_2SiF_6 + 18-crown-6-ether, H: K_2SiF_6 + 18-crown-6-ether,

I: NaF + 18-crown-6-ether

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Chapter 2: Synthesis and Rearrangement of Silsesquioxane and Spherosilicate Cages

2.0 Introduction

The aim of this initial work was to develop a high yielding route for the synthesis of silsesquioxanes, such as T_8R_8, $T_{10}R_{10}$ and $T_{12}R_{12}$, where R could be a hydrocarbon, aryl, amino or mercapto chain. Once successful in synthesising these cages, the characterisation of these highly symmetrical cages would not be difficult using ^{29}Si NMR[1] and Matrix-Assisted Laser Desorption/Ionisation Time-of Flight (MALDI-TOF)[2] mass spectroscopy. In the second stage, the rearrangement reaction of silsesquioxane cages was studied in order to understand the underlying chemistry of these cages. Different kinds of catalysts were employed, such as electrophiles, oxygen nucleophiles and fluoride ion. The biggest challenge is isolation and characterisation of the reaction products, although ^{29}Si NMR is particularly diagnostic. Gas Chromatography (GC) proved not to be very useful for characterisation because the cages decompose at the high temperature required for vaporisation. However, High Performance Liquid Chromatography (HPLC) and Gel Permeation Chromatography (GPC) appeared to be appropriate techniques.[3]

A similar approach was taken for the spherosilicate cages, such as Q_6R_6 and Q_8R_8. The synthesis of spherosilicates in high yield has been reported and thus we studied the degradation and rearrangement of these Q cages. Again, different catalysts were employed for degradation and rearrangement of the spherosilicate cages. The characterisation and isolation was again the greatest challenge. As with the silsesquioxanes, ^{29}Si NMR and HPLC were the most useful techniques.

2.1 Synthesis of Silsesquioxane Cages

In the first example of such a study, Sprung and co-workers reported[4] that partial hydrolysis of alkyltrialkoxysilanes gave hexa and octasilsesquioxanes with an acidic or a basic catalyst. However the silsesquioxane cages were only obtained in trace amounts.

Subsequently, Barry and co-workers reported[5] that octasilsesquioxanes could be synthesised by the hydrolytic condensation of trichloroalkylsilanes. However, the yield of the silsesquioxane cages was very low. Although the method of hydrolysis of the trichloroalkylsilane was later modified,[6,7,8,9] the yield of the octasilsesquioxane, T_8R_8, was always lower than 40%. There was also a great deal of resin or other siloxane by-products produced by these hydrolytic condensations.

As discussed in Section 2.2.1, an alternative route to obtain octasilsesquioxanes with a range of functionalities on the core is a two-step process. The first step is to synthesise the octahydrosilsesquioxane, T_8H_8,[6,7,9] which can be easily isolated and purified as a needle shape crystals by recrystallisation from hexane, although the yield is still low. The second step is to funtionalise the Si-H with a variety of alkenes by hydrosilylation.[9] The yield of the hydrosilylation step is very high, up to 99% with a platinum catalyst. However, with terminal alkenes, hydrosilylation can lead to either α-addition or β-addition, depending on the alkene and it is often difficult to isolate the pure α- or β- addition products. Furthermore, depending upon the reactivity of the silane, the alkene and the catalyst, incomplete hydrosilylation of T_8H_8 core is sometimes observed, leading to cages with only 6 or 7 arms. This also provides another hurdle to purification.

To sum up, both hydrolysis of a trihalosilanes or hydrosilylation of T_8H_8, lead to low yields and complex mixtures, depending upon solvents, temperature, catalyst, etc. and thus new routes to silsesquioxane cages are still desirable.

In this section we will discuss the reaction of a variety of alkyltrialkoxysilanes with tetra-*n*-butylammonium fluoride solution, TBAF, containing 5% water. A range of high molecular weight silsesquioxane cages was successfully produced, such as T_8R_8, $T_{10}R_{10}$ and $T_{12}R_{12}$. In particular, the reaction gave significantly higher yields for the synthesis of octasilsesquioxanes, T_8R_8, using a simple one-pot route.

2.1.1 Synthesis of Alkyltrialkoxysilanes

Most of the alkyltrialkoxysilanes are commercial available, such as methyltriethoxysilane, phenytriethoxysilane and allyltriethoxysilane. However, some of the alkyltrialkoxysilanes are expensive, or not available. Thus, to expand the variety of alkyltrialkoxysilanes that we can use to make T_8R_8 cages, we had to develop high yielding routes to such compounds.

2.1.1.1 Using trichlorosilanes

The synthesis of alkyltrialkoxysilanes can be easily achieved by the reaction of alkyltrichlorosilanes and an alcohol, Scheme 2.1.

$$RSiCl_3 + R'OH \xrightarrow[THF]{NEt_3} RSi(OR')_3 + H^+NEt_3Cl^-$$

Scheme 2.1

Cyclopentyltrichlorosilane was used as a model for the synthesis of alkyltriethoxysilanes, as shown in Scheme 2.2. Ethanol was dissolved in dry THF and triethylamine was added. The mixture was stirred for a couple of minutes and then a solution of the trichlorosilane was added drop-wise. A white solid precipitated out, during addition of the cyclopentyltrichlorosilane solution. The reaction mixture was stirred for a further 4 hours after which the white solid was filtered off. After removal of the solvent from the filtrate, cyclopentyltriethoxysilane **2.1** was obtained as a yellow liquid. The product was shown to be sufficiently pure for use in the next reaction on the basis of its NMR spectra.

$$(c\text{-}C_5H_9)SiCl_3 + EtOH \xrightarrow[THF]{NEt_3} (c\text{-}C_5H_9)Si(OEt)_3 + H^+NEt_3Cl^- \quad (2.1)$$

Scheme 2.2

This synthetic route was used to prepare a range of alkyltriethoxysilanes, such as cyclohexyltriethoxysilane, benzyltriethoxysilane and *p*-methoxyphenyl-

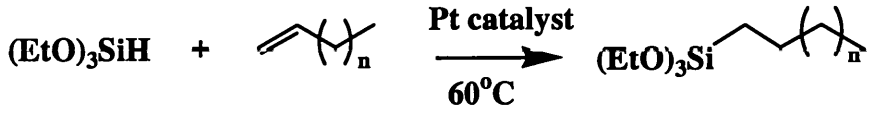
propyltriethoxysilane, from the corresponding trichlorosilanes. The yields of these reactions are given in Table 2.1.

Table 2.1 The yields of alkyltriethoxysilane from the corresponding trichlorosilane

Starting Material	Product	Yield (%)
c-$C_5H_9SiCl_3$	c-$C_5H_9Si(OEt)_3$ **2.1**	77.7
c-$C_6H_{11}SiCl_3$	c-$C_6H_{11}Si(OEt)_3$ **2.2**	85.8
$C_6H_5CH_2SiCl_3$	$C_6H_5CH_2Si(OEt)_3$ **2.3**	82.8
p-$CH_3OC_6H_4(CH_2)_3SiCl_3$	*p*-$CH_3OC_6H_4(CH_2)_3Si(OEt)_3$ **2.4**	86.0

2.1.1.2 Hydrosilylation

An alternative method for the synthesis of alkytriethoxysilanes is hydrosilylation, involving reaction of triethoxysilane with an alkene in the presence of a platinum catalyst, as shown in Scheme 2.3.[9,10]

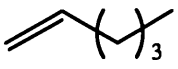
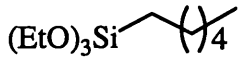
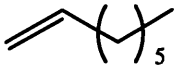
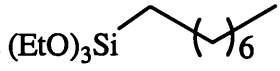
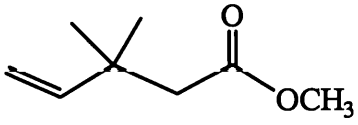
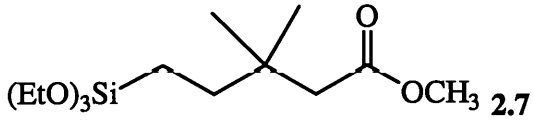


Scheme 2.3

Hydrosilylation could give rise to either α-addition and/or β-addition products. β-Addition is favoured if there are electron rich atom attached to the silicon atom. Thus, the presence of three electron rich oxygen atoms in the triethoxysilane will favour the formation of the β-addition product. Three alkenes were used for hydrosilylation, 1-heptene, 1-octene and methyl 3,3-dimethylpent-4-enoate. Triethoxysilane and the alkene were placed in a small vial and the platinum catalyst was added. The mixture was heated at 60°C for about 48 hours. The reaction was followed by IR until the Si-H peak at 2156 cm^{-1} had completely disappeared. The product was purified by flash column chromatography to remove the

platinum catalyst and any unreacted starting materials. The yield of the hydrosilylations is shown in Table 2.2.

Table 2.2 The yield of alkyltriethoxysilane from hydrosilylation

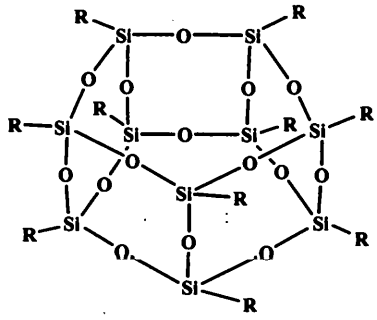
Alkene	Product	Yield (%)
	 **2.5**	94.7
	 **2.6**	91.0
	 **2.7**	90.4

2.1.2 Reaction of Alkyltrialkoxysilanes with tetra-*n*-butylammonium fluoride

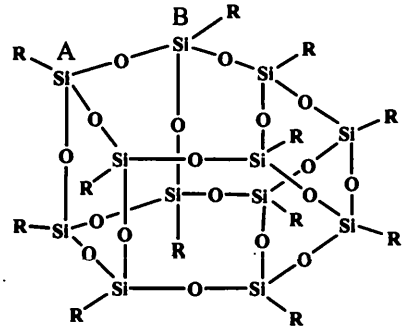
^{29}Si NMR is a powerful diagnostic technique for the characterisation of silsesquioxane cages. The chemical shift of the silicon atom varies over a wide range depending upon the atom or groups attached to the silicon.[1] In particular, Marsmann and co-worker has developed equations[3] to show the relationship between the ^{29}Si NMR chemical shifts in T_8R_8, $T_{10}R_{10}$ and $T_{12}R_{12}$ cages. The $T_{10}R_{10}$ cage **2.8** is made up of two condensed Si-O five-membered rings, so that there is only one silicon environment, giving rise to only one peak in the ^{29}Si NMR. The ^{29}Si chemical shift in $T_{10}R_{10}$ has been shown to be a function of the corresponding T_8R_8 chemical shift, as shown in Equation 2.1.

Equation 2.1: $\delta T_{10}R_{10} = 1.028 \times \delta T_8R_8$

$T_{12}R_{12}$, can exist in two isomeric forms. One isomer of $T_{12}R_{12}$ is made of two condensed Si-O six-membered rings, which would show only one ^{29}Si NMR peak. The second isomeric form is much more favourable and is readily formed by the rearrangement of T_8R_8 with bases. This $T_{12}R_{12}$ **2.9** contains two different silicon environments.



(2.8)



(2.9)

One type of silicon atom, A, is linked with two Si-O four-membered rings and one Si-O five-membered ring. Another kind of silicon environment is B involved with one Si-O four-membered ring and two Si-O five-membered rings. The relationship of the chemical shifts of silicon A and B with the corresponding T_8R_8 is given by Equation 2.2 and Equation 2.3. These equations are very useful for the identification of T_8R_8, $T_{10}R_{10}$ and $T_{12}R_{12}$ silsesquioxane cages.

Equation 2.2: $\delta T_{10}R_{10}A = 1.025 \times \delta T_8R_8$

Equation 2.3: $\delta T_{10}R_{10}B = 1.064 \times \delta T_8R_8$

The reaction of a variety of trialkoxysilanes with TBAF was carried out as shown in Scheme 2.4.

$$RSi(OR')_3 \xrightarrow[\text{Solvent}]{\text{TBAF}} \text{Condensation products}$$

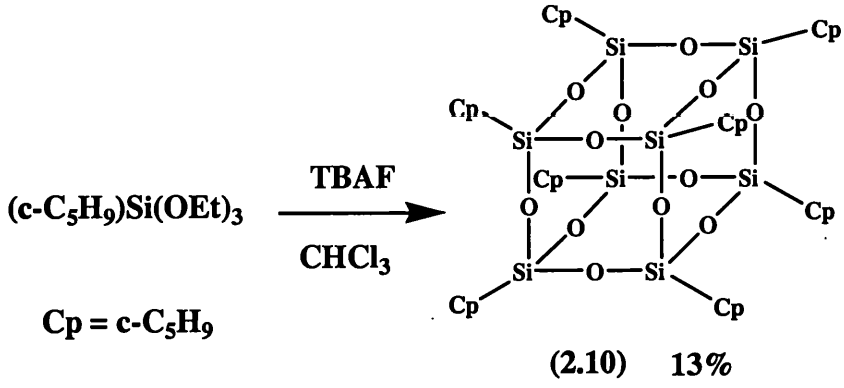
Scheme 2.4

A series of R groups, R = methyl, vinyl, allyl, *n*-hexyl, *n*-octyl, methyl 3,3 dimethylpent-4-enoate, *p*-methoxyphenylpropyl, cyclopentyl, cyclohexyl, phenyl, 3-aminopropyl, 3-mercaptopropyl and benzyl, were used in the reaction with TBAF. Alkyltrialkoxysilane was treated with TBAF in an organic solvent and the reaction mixture stirred at room temperature overnight or for longer. It was found that alkyltrialkoxysilane readily

oligomerised to give well-defined high molecular mass silsesquioxane cages, such as T_8R_8, $T_{10}R_{10}$ and $T_{12}R_{12}$.

2.1.2.1 Reaction of cyclopentyltriethoxysilane

The octacyclopentylsilsesquioxane cage has been well characterised and so the reaction of cyclopentyltriethoxysilane with TBAF was chosen as a model reaction to determine the best conditions for the formation of T_8R_8 cages. The reaction was carried out as shown in Scheme 2.5.



(2.10) 13%

Scheme 2.5

Chloroform was chosen because it is a good solvent for solublising the silsesquioxanes. Thus the reaction was performed in chloroform with a mole ratio of 1:0.5 of the cyclopentyltriethoxysilane to TBAF. The reaction mixture was stirred at room temperature for 24 hours and the reaction mixture analysed by ^{29}Si NMR. The NMR spectrum contained a group of peaks in the T-Si region between -66 and -68 ppm, but no single sharp peaks. The shape of these peaks suggests the formation of a resin rather than a single product. One possible reason is that the cyclopentyl group can be considered as a relatively bulky group such that the formation of a cage framework would be slow. Thus, the reaction mixture was stirred for a further 24 hours. ^{29}Si NMR analysis of the reaction mixture revealed a group of single sharp peaks between -60 and -70 ppm. The reaction was stopped and extracted with water in order to remove the TBAF. A white solid gel residue was obtained after separation of the organic layer and removal of the solvent. This residue

was analysed by ^{29}Si NMR, as shown in Figure 2.1. There is a group of peaks between -60 and -70 ppm, which could not be unambiguously identified. However, it is obvious that the octacyclopentylsilsesquioxane cage **2.10**, CpT_8, is formed giving rise to the sharp peak at -66.55 ppm. Since the CpT_8 does not dissolved in acetone, the residue mixture was extracted with acetone to give a white solid product with a ^{29}Si NMR containing a single peak at -66.55 ppm. This, together with the ^{1}H and ^{13}C NMR, strongly suggests that the white product is CpT_8. To confirm the identity of this solid compound, it was spiked with a known standard sample of CpT_8 obtained from Dow Corning UK. This again gave a single peak in the ^{29}Si NMR. This reaction produced CpT_8 in 13.4% yield. The rest of the acetone fraction was collected and gave a gel after removal of the solvent. The ^{29}Si NMR spectra in Figure 2.2 still shows a group of sharp peaks between -60 and -72 ppm. The peaks with a downfield chemical shift, from -60 to -64 ppm suggest the presence of some Si-OH groups, which are attached to the silsesquioxane cage. The upfield peaks with a chemical shift from -66 to -72 ppm may arise from high molecular weight cage formation.

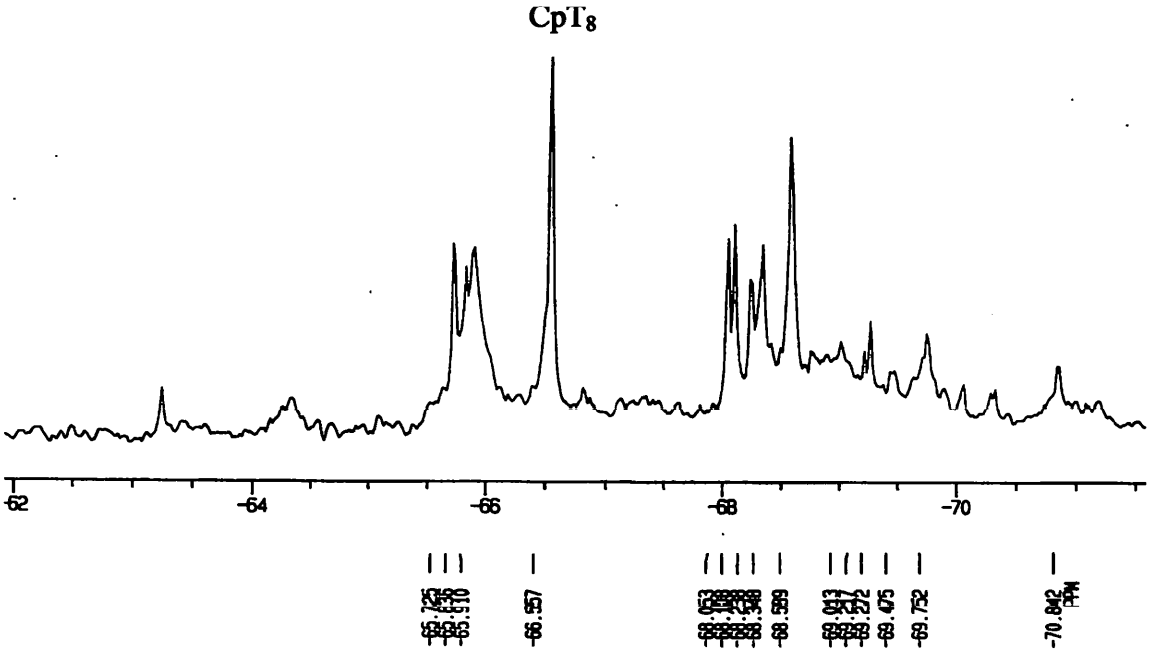


Figure 2.1

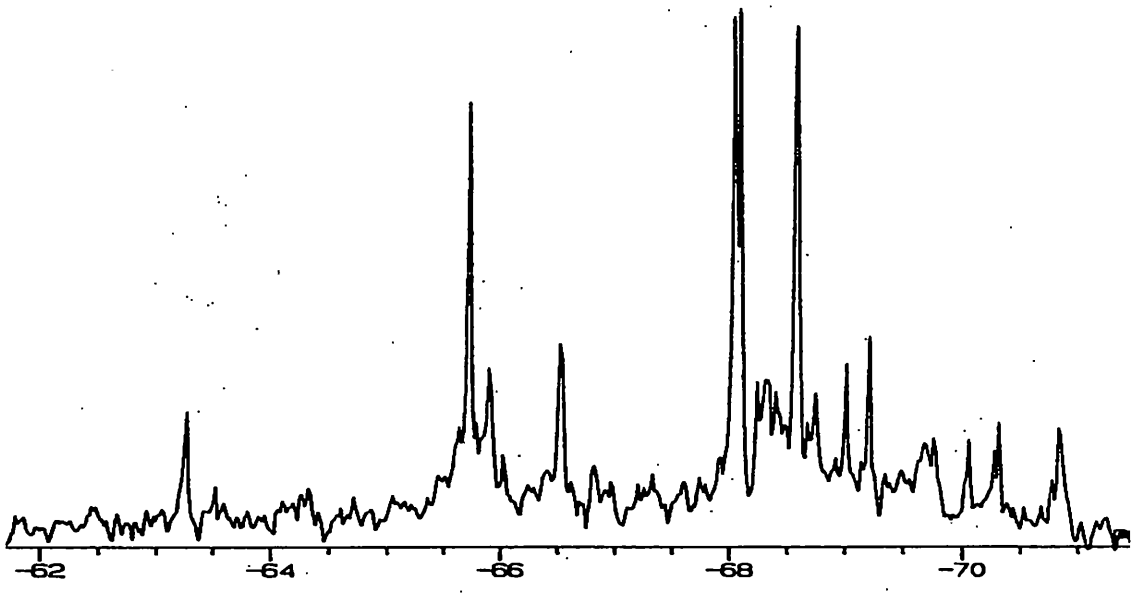


Figure 2.2

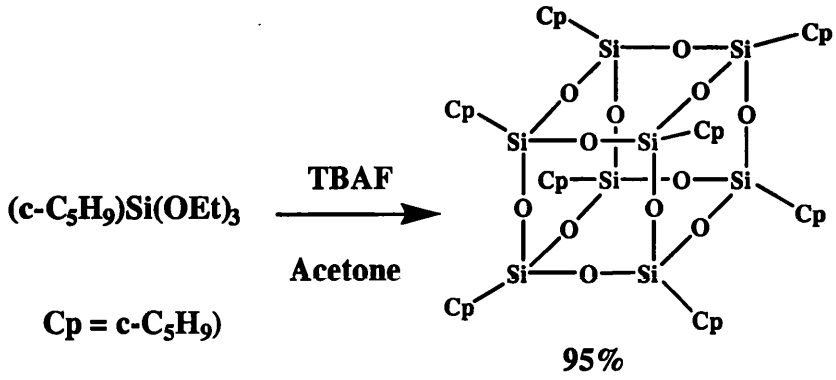
It may be expected that the condensation of cyclopentyltriethoxysilane could lead to silanol species associated with the Si-O-Si frameworks because there is some water present in the TBAF solution in THF. However, it still remained a question whether the CpT_8 cage was formed before or after the formation of these Si-OH cage compounds.

To test this, the reaction was repeated with an excess of TBAF solution. If the silicon frameworks associated with the Si-OH groups were intermediates in the formation of the CpT_8 cage, the excess TBAF should result in the yield of CpT_8 being higher than before. On the other hand, there should not be very much CpT_8 cage left in the reaction mixture if the silicon frameworks associated with the Si-OH groups are formed by the cleavage of the Si-O-Si linkage of the CpT_8 cage. Thus, cyclopentyltriethoxysilane was stirred with 2 equivalents of TBAF for 24 hours at room temperature. ^{29}Si NMR analysis of the reaction mixture showed a single peak at -66.55 ppm and a quintet at -113.99 ppm. The peak at 66.55 ppm indicated the formation of the CpT_8 cage and the quintet at -113.99 ppm showed the formation of $RSiF_4^-$ species. The reaction mixture was then extracted with water to remove the TBAF and the organic solution evaporated under vacuum to give a white solid gel. This solid gel residue was extracted with a mixed solvent of acetone and

hexane to give a white solid. The yield of the CpT_8 cage (23.4%) was much higher than before. This suggested that the Si-OH silicon compounds may be precursors for the formation of CpT_8 cage.

In order to study this rearrangement further, the reaction was slowed down by reducing the quantity of the TBAF. Thus, cyclopentyltriethoxysilane was dissolved in chloroform with 0.25 equivalents of TBAF and stirred at room temperature. The reaction mixture was analysed by ^{29}Si NMR every 2 hours. Unfortunately, the NMR data gave little information for the reaction process apart from showing a peak for the starting material even after 48 hours. The reaction mixture was stirred for a longer time and the mixture was analysed by ^{29}Si NMR every 4 hours. After 72 hours stirring the ^{29}Si NMR spectrum showed the presence of a group of peaks between -60 and -72 ppm, which had a similar pattern to those shown in Figure 2.1. There is no evidence for the formation of the hexacyclopentylsilsesquioxane cage, CpT_6, in the reaction, which has a ^{29}Si NMR chemical shift about -54 ppm. We might expect the CpT_6 to be formed before the CpT_8 cage. However, the ring strain in the CpT_6 may prevent its formation. Since the Si-O four-membered ring is thermodynamically more stable than the Si-O three- membered ring then the construction of CpT_8 cages from CpT_4 rings may occur more readily then the construction of CpT_6 cages from CpT_3 rings.

Since CpT_8, has a low solubility in many solvents, one strategy could be for the CpT_8 cage to be precipitated out as soon as it formed. Thus avoiding the possibility of the CpT_8 cage being involved in any further reaction. Thus acetone was employed as a solvent instead of chloroform as shown in Scheme 2.6.



Scheme 2.6

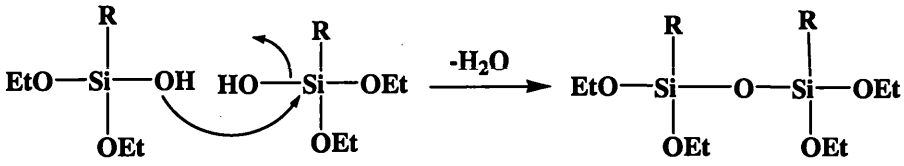
Cyclopentyltriethoxysilane was dissolved in acetone, then 0.5 equivalents of TBAF was added and the reaction mixture stirred at room temperature. A white solid precipitated out after only 30 minutes stirring. This solid was filtered and analysed by NMR, which confirmed that this solid was pure CpT_8. The yield of CpT_8 obtained in half an hour had increased to 40.1%. The filtered liquid was collected and continued stirring and filtered whenever the white solid was observed in the mixture. The yield was thus increased to 80.3%. The reaction was repeated on a large scale and the yield of the product, CpT_8, was increased to 94.8% after 4 hours stirring.

Further investigations, using other solvents such as THF, also showed that CpT_8 could be obtained in high yields and within a relatively short reaction time. Table 2.3 showed the comparison of the yield of CpT_8 from the different solvents. Further investigations of different solvent systems, such as pyridine, toluene, hexane, and ether, have been subsequently carried out in our research group.

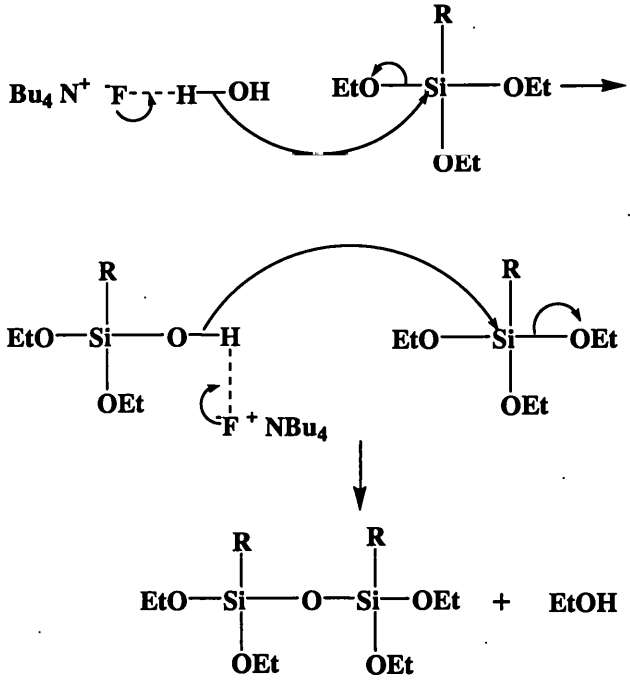
Table 2.3 The yield of CpT_8 from different solvents

Solvent	Reaction time (hour)	Yield (%) of T_8
Chloroform	48	13.4
THF	12	23.4
Acetone	4	94.8

In order to understand the formation of CpT_8 from the monomer, cyclopentyltriethoxysilane, the reaction mechanism was investigated. We would expect the condensation of alkytriethoxysilane to involve reaction with water to produce a silanol, Si-OH, which then undergoes condensation, as shown in Scheme 2.7.[4,11-13] Since there is water (5%) in the TBAF solution, it is this that produces the silanol groups in the reaction. ^{29}Si NMR of the reaction mixture confirmed the presence partial cages with silanol groups. The first step involves cleavage of the Si-O bond of the alkytriethoxysilane, by a nucleophile, a complex of the water with the fluoride ion, as shown in Scheme 2.8.



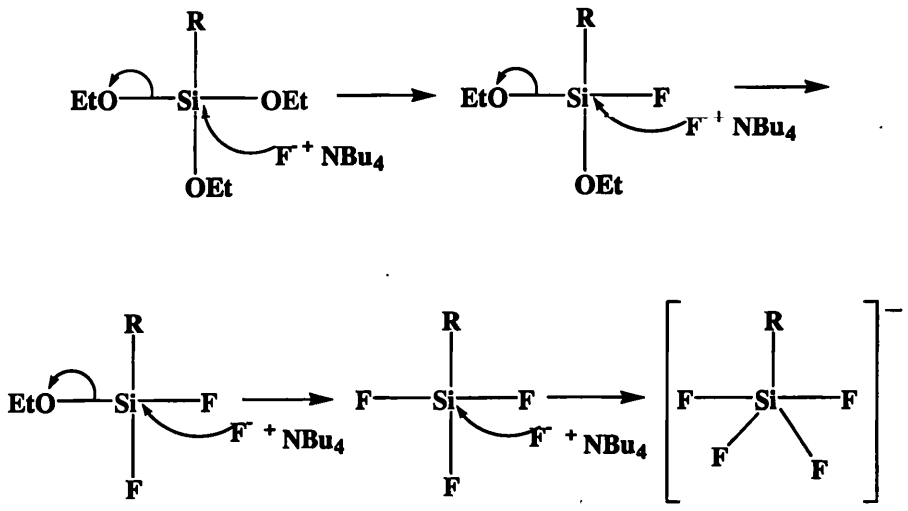
Scheme 2.7



Scheme 2.8

The formation of ethanol from the EtO^- leaving group occurs and the fluoride ion can be recycled for further condensation. Once all of the water has been used up, the condensation of the alkyltriethoxysilane stops. At this stage, TBAF is dry enough to react directly with

the remaining alkytriethoxysilane and lead to the formation of fluorosilicon compounds, such as $RSiF_3$, $RSiF_4^-$, $RSiF_5^{2-}$ and even $RSiF_6^{3-}$ species, Scheme 2.9.

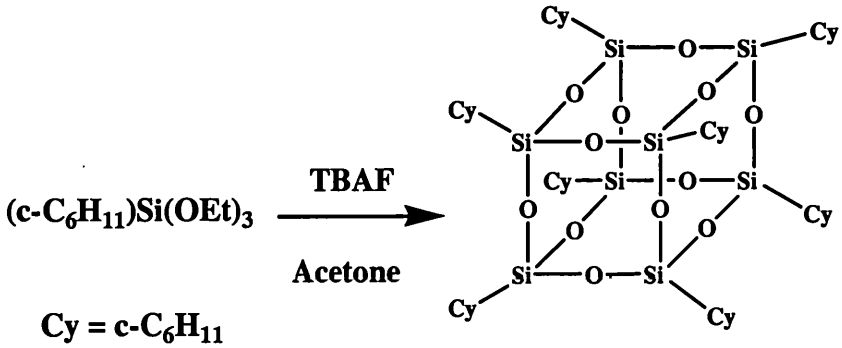


Scheme 2.9

If the reaction is repeated with tetra-*n*-butylammonium chloride, again adding some water, no reaction is observed, confirming the importance of the fluoride ion in hydrogen bonding with the water and this increases the nucleophilicity of the oxygen atom. To confirm this reaction mechanism a further experiment was undertaken. The condensation was carried out using an excess of water, which should lead to silsesquioxanes with silanol groups as the main products. Thus, the reaction of cyclopentyltriethoxysilane with TBAF was repeated as before in chloroform, but using a 20 fold of water. After 3 days stirring, the reaction gave partial cage products with Si-OH groups, giving rise to a range of peaks between -40 and -68 ppm in the ^{29}Si NMR, which confirmed the existence of water in the TBAF solution involving with the condensation of cyclopentyltriethoxysilane.

2.1.2.2 Reaction of cyclohexyltriethoxysilane

The cyclohexyl group has similar properties to the cyclopentyl group and the octacyclohexylsilsesquioxane, CyT_8, has been well characterised. Since the CpT_8 could be obtained in high yield in acetone, the reaction of cyclohexyltriethoxysilane with TBAF was performed in acetone, as shown in Scheme 2.10.



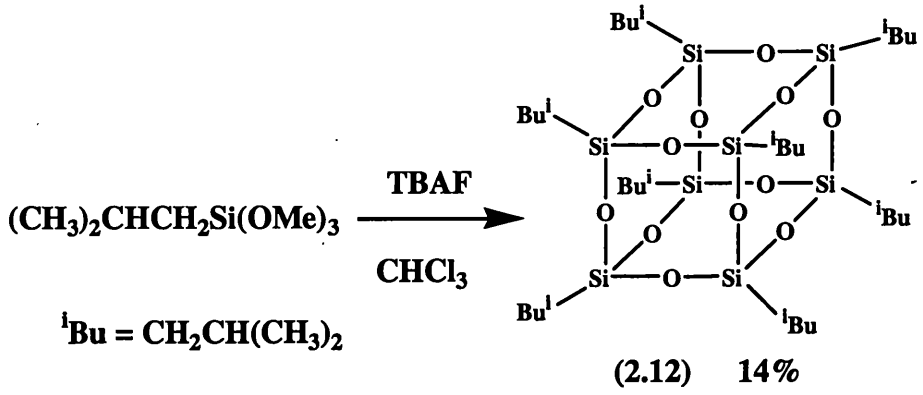
Scheme 2.10

Cyclohexyltriethoxysilane was dissolved in acetone then TBAF was added to the solution and the reaction mixture stirred at room temperature. A white solid was observed in the mixture after 10 minutes. The mixture was filtered after 30 minutes stirring to give a white solid. This solid was analysed by ^{29}Si NMR, which showed the presence of a single peak at -68.69 ppm and identical to the chemical shift obtained for CyT_8 **2.11**. After half an hour the yield of CyT_8 was 67.2%, and the filtrated was stirring for further 4 hours to give a total of 83.6% CyT_8.

2.1.2.3 Reaction of iso-butyltrimethoxysilane

Most octaalkylsilsesquioxanes, T_8R_8, with linear carbon chains on the core are gels or waxes, however, the T_8R_8 can be a solid or even crystalline when a relatively bulky group is attached to the core. Octa-*iso*-butylsilsesquioxane, *iso*-butylT_8, gives good crystals, which are insoluble in acetone. Thus, it may be possible to obtain *iso*-butylT_8 in high yield if the reaction of *iso*-butyltrimethoxysilane with TBAF was carried out in acetone. Thus, acetone was used as solvent and the reaction mixture was stirred at room temperature. However, a solid did not precipitate out from the mixture. The mixture was stirred for a further 24 hours, then analysed by ^{29}Si NMR which revealed three groups of peaks, between -50 and -60 ppm, between -65 and -69 ppm and a set of quintet at -113.99 ppm. Since there are so many peaks in the spectrum, it was too difficult to identify all the components. However, this range of peaks suggested the formation of some Si-OH groups

within the Si-O-Si framework and some high molecular mass silsesquioxanes together with $RSiF_4^-$ species. It also hints that the reaction had occurred too quickly in acetone leading to a random Si-O-Si framework rather than a well-defined silsesquioxane. It may be possible to slow the reaction down using a different solvent or its *iso*-butyltriethoxysilane. Because *iso*-butyltriethoxysilane is not commercially available, so the reaction was studied with a different solvent system. Thus chloroform was used for the reaction, since chloroform had worked well for the reaction of cyclopentyltriethoxysilane, even though the yields of the octasilsesquioxane were lower than in acetone. Therefore, the reaction of *iso*-butyltrimethoxysilane was repeated in chloroform as shown in Scheme 2.11.



Scheme 2.11

The reaction was carried out by dissolving *iso*-butyltrimethoxysilane in chloroform, then adding TBAF and stirring the reaction mixture at room temperature for 24 hours. The ^{29}Si NMR spectrum of a sample of this solution, Figure 2.3, shows a group of peaks between -67 and -71 ppm indicating that high molecular weight T-Si frameworks were formed. The two major peaks at -68.44 and -70.47 ppm correspond to the octa and deca-*iso*-butylsilsesquioxane. The triplet at -113.99 ppm indicates a Si-F coupling corresponding to a R_2SiF_2 fragment. However, the chemical shift at -113.99 ppm is at too high field for R_2SiF_2, which should be more downfield than -70 ppm.[14] On the other hand, a chemical shift at -113.99 ppm suggests a $RSiF_4^-$ species. Although the NMR spectrum showed as a

triplet, it could be part of a quintet where the two outer peaks are lost in the noise of the base line. These peaks disappeared on washing with water.

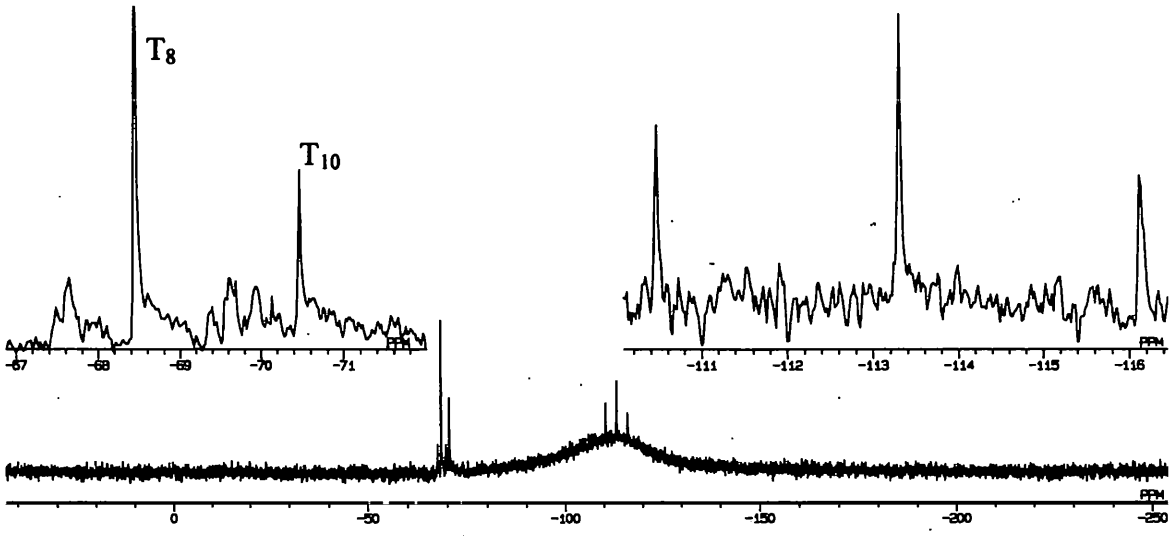


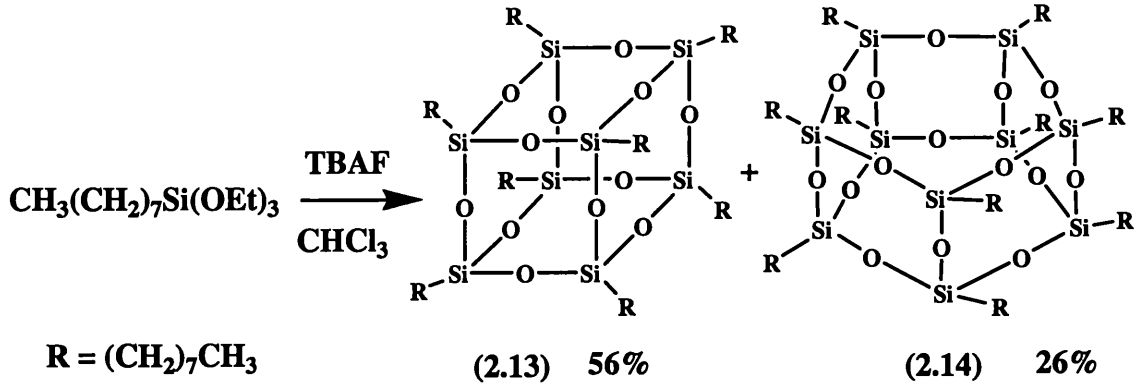
Figure 2.3

In order to stop the reaction and remove the TBAF, the reaction mixture was extracted with water. The organic layer separated and a solid gel was obtained after removal of the solvent. The *iso*-butylT_8 cage is not expected to dissolve in acetone. Thus the solid gel was extracted with a mixed solvent of acetone and chloroform. A white solid was obtained, which could be recrystallised from chloroform. This crystal was analysed by ^{29}Si NMR which showed a single sharp peak at -67.90 ppm identical to that of *iso*-butylT_8 **2.12**. The ^{1}H and ^{13}C also showed identical chemical shifts for the *iso*-butyl groups on the core. To further confirm the identity of this product, the ^{29}Si NMR was repeated using a known sample of *iso*-butylT_8 to spike the product. The NMR spectra showed still only a single sharp peak at -67.90 ppm. This indicates that *iso*-butyltrimethoxysilane can be converted to a high molecular weight silsesquioxane cage, *iso*-butylT_8 and gave 14.7% yield using TBAF in chloroform. The remaining product from the extraction was also analysed. The ^{29}Si NMR showed that the peaks at –113.99 ppm had disappeared leaving a number of distinct peaks in the T-Si region between -57 and -70 ppm. The group of peaks between -57 and -65 ppm indicated the formation of some partial cages with silanol groups. The

group of peaks between -65 and -70 ppm correspond to the T-Si region, indicating high molecular weight cages were produced alongside the formation of *iso*-butylT_8. Comparison of the two NMR spectra shows that more peaks appeared in the mixture after washing because of concentration.

2.1.2.4 Reaction of octyltriethoxysilane

Octyltriethoxysilane has a linear carbon chain rather than a bulky group. The octa and decaoctylsilsesquioxane cages, OctylT_{10} and OctylT_{12}, have been well characterised with ^{29}Si NMR chemical shift of -66.74 and -68.68 ppm respectively.[3,15] Thus, it would be very easy to determine if any OctylT_{10} and OctylT_{12} cage is formed in the reaction of octyltriethoxysilane with TBAF . The previous works, with *iso*-butyltrimethoxysilane and TBAF in acetone gave a very complicated mixture since condensation occurred too rapidly. Reaction of octyltriethoxysilane with TBAF may be expected to be faster than with *iso*-butyltrimethoxysilane, since the linear chain provides less steric hindrance at the silicon, thus chloroform was chosen for this reaction, as shown in Scheme 2.12.



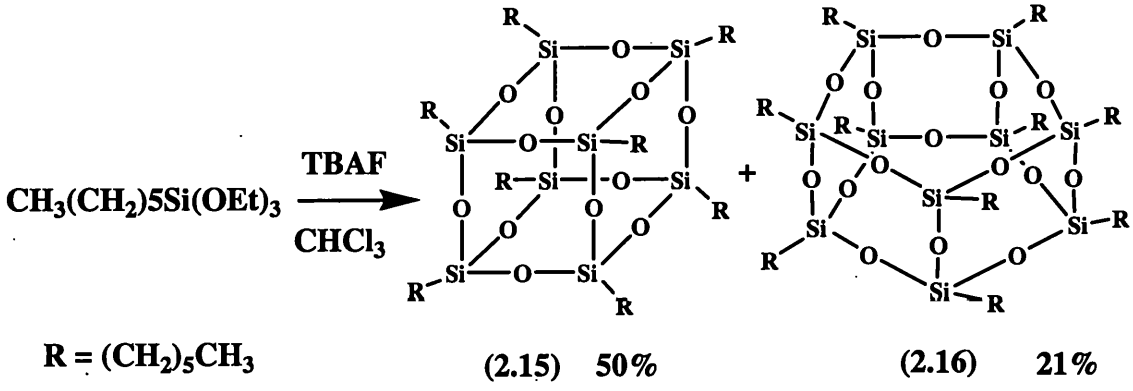
Scheme 2.12

Octyltriethoxysilane was treated with TBAF in chloroform and the mixture stirred at room temperature for 24 hours, then extracted with water. A colourless gel was obtained after removal of the solvent from the organic fraction. This gel was analysed by ^{29}Si NMR, which revealed two main peaks at -66.64 ppm and -68.57 ppm. Comparison of the

chemical shift with those of the OctylT_8 and OctylT_{10}, published by Marsmann and co-workers, confirmed the formation of the OctylT_8 **2.13** and OctylT_{10} **2.14** cages from the reaction of octyltriethoxysilane with TBAF. There is also a group of small peaks between -65 and -67 ppm, still within the T-Si region. This suggests that other high molecular weight silsesquioxane cages are formed along with the OctylT_8 and OctylT_{10}. From the ^{29}Si NMR, The OctylT_8 was obtained in 56% and OctylT_{10} in 26% yield.

2.1.2.5 Reaction of hexyltriethoxysilane

Hexyltriethoxysilane was chosen since it is similar in size, at the silicon, to the octyl group and because the octahexylsilsesquioxane has been well characterised.[15] Thus, the reaction of hexyltriethoxysilane with TBAF was carried out as shown in Scheme 2.13.



Scheme 2.13

As with octyltriethoxysilane, chloroform was chosen as the solvent for the reaction. Thus, hexyltriethoxysilane was dissolved in chloroform followed by addition of TBAF. The reaction mixture was stirred at room temperature for 24 hours after which a sample was analysed by ^{29}Si NMR after removal of the solvent. The ^{29}Si NMR showed the peak at -44.98 ppm corresponding to the starting material has disappeared and a group of peaks between -66 and -68 ppm has appeared. Thus, the reaction was stopped by extraction with water to remove TBAF. The organic layer was separated and a colourless gel was obtained after removal of the solvent.

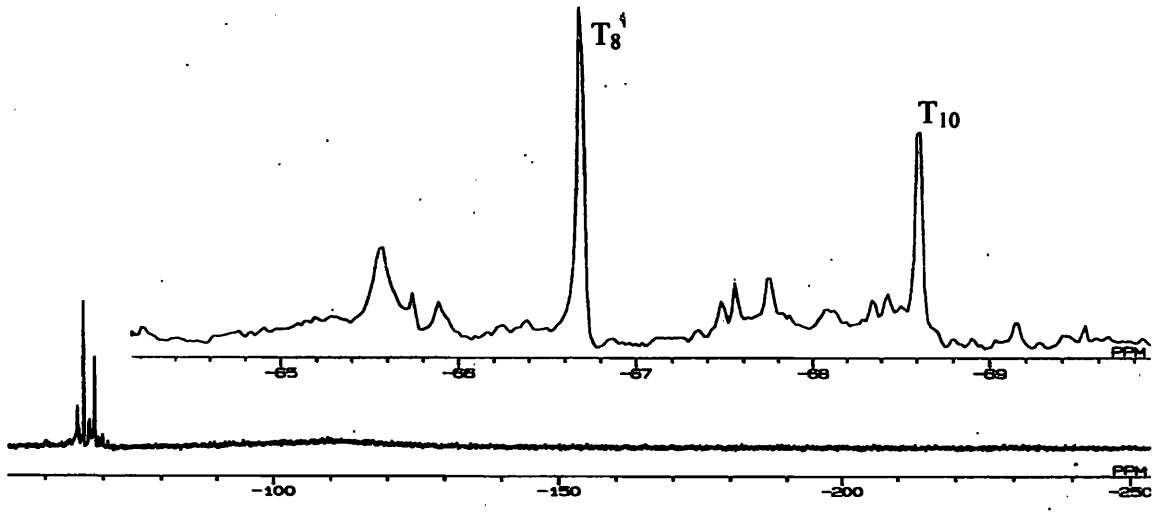


Figure 2.4

The product was analysed by ^{29}Si NMR, Figure 2.4, which exhibits a group of peaks between -65 and –69 ppm, indicating a T_7 silicon environment. There are two major peaks at -66.68 and -68.62 ppm. The literature ^{29}Si NMR chemical shift for octahexylsilsesquioxane, HexylT_8, is -66.63 ppm [3,15] and the chemical shift of decahexylsilsesquioxane, HexylT_{10}, should be about 2 ppm to higher field than the octasilsesquioxane. This suggests the two major peaks in the NMR spectra of the reaction mixture correspond to HexylT_8 **2.15** and HexyT_{10} **2.16**. The yield of HexylT_8 and HexylT_{10} is 50% and 21% based on NMR. There also appears to be a small amount of other T_7 cages as an evident by the remaining peaks between -65 and -67 ppm. However, these peaks could not entirely be resolved. The product was also analysed by MALDI-TOF mass spectroscopy, as shown in Figure 2.5.

This confirms that HexylT_8 and HexylT_{10} were obtained with the fragment at *m/z* 1097.70 corresponding to the HexylT_8 and the fragment at *m/z* 1373.83 to the HexyT_{10}. Other fragments at *m/z* 1226, 1246, 1502, 1521, 1650 and 1795, indicate that other high molecular weight silsesquioxane cage products are also obtained from this reaction. Separation of the product using chromatography was attempted but was unsuccessful since they have similar polarity.

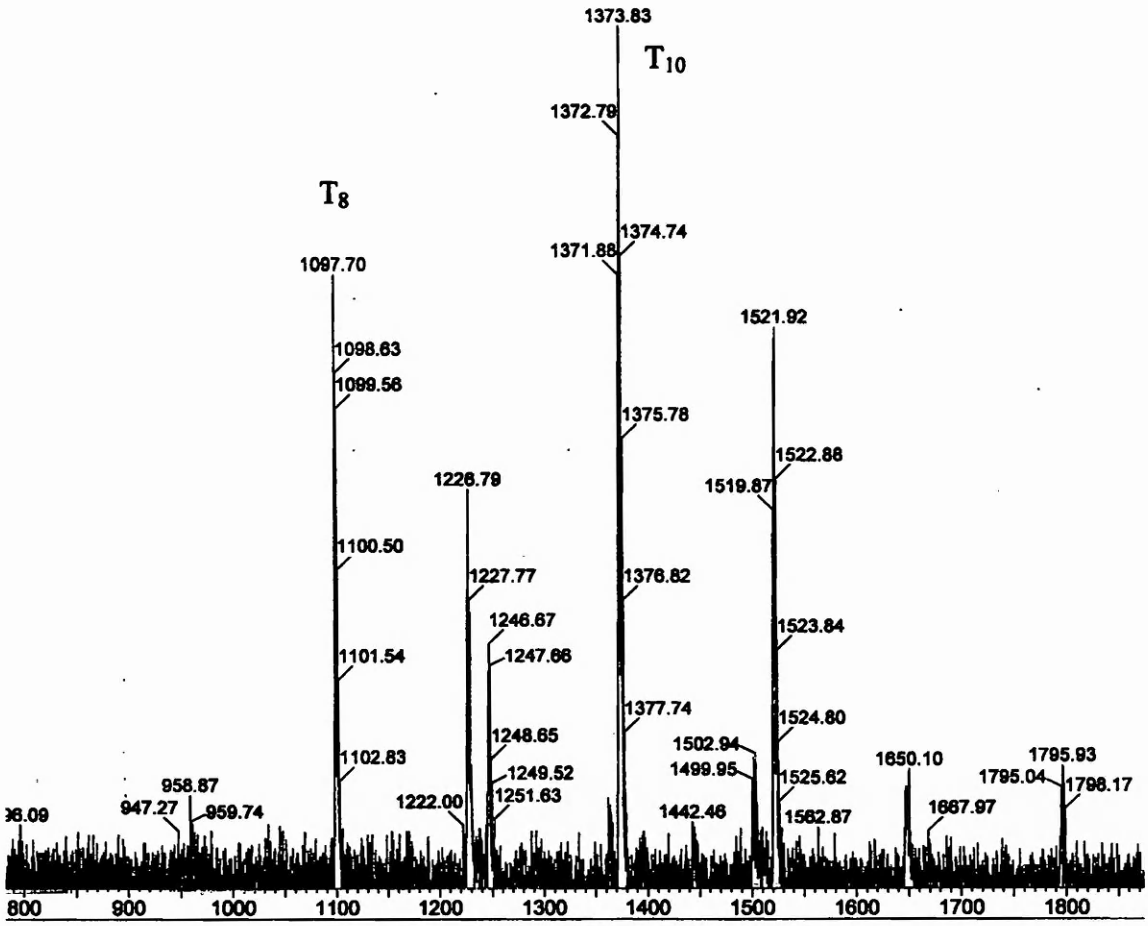


Figure 2.5

Comparison of the reactions of octyltriethoxysilane and hexyltriethoxysilane with TBAF shows that the ratio of decaalkylsilsesquioxane to octaalkylsilsesquioxane is greater for the hexyl compounds than the octyl compounds. This suggests that the OctylT_8 is rearranged to OctylT_{10} more slowly than the HexylT_8, presumably as a result of the longer chain hindering attack by the nucleophile.

2.1.2.6 Reaction of methyltriethoxysilane

The methyl group is the smallest of all the alkyl groups. Thus we might expect the condensation of methyltriethoxysilane to be very fast.[11,12] On the other hand, the solubility of octamethylsilsesquioxane is very poor, even in chloroform and dichloromethane. Thus,

methylsilsesquioxanes should be easily isolated from the reaction mixture by precipitation. So the reaction was performed in acetone, as shown in Scheme 2.14.

$$CH_3Si(OEt)_3 \xrightarrow[\text{Acetone}]{\text{TBAF}} \text{Resins}$$

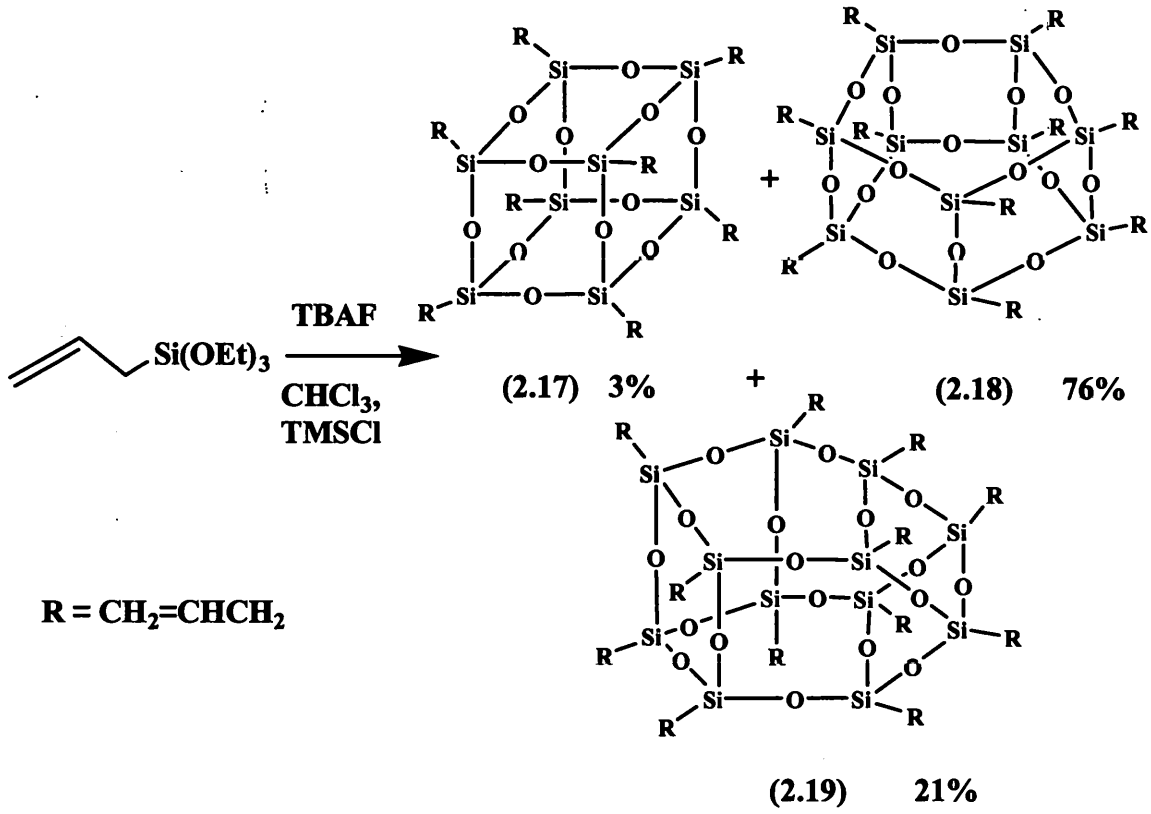
Scheme 2.14

Methyltriethoxysilane was dissolved in acetone followed by the addition of TBAF. The mixture was stirred at room temperature for 24 hours during which time a white solid precipitated out. Unfortunately this solid did not dissolve in any common solvents, including chloroform and cyclohexane. Thus, solution NMR data could not be obtained for the characterisation of this solid product. However, since reaction should be fast, we might predict that the methyltriethoxysilane would readily form a resin rather than give well-defined silsesquioxane. That is, the condensation would be too rapid and the methyl group exerts too little control to give an organised Si-O-Si framework.

2.1.2.7 Reaction of allyltriethoxysilane

In order to prepare silsesquioxanes with a range of functionality, allytriethoxysilane was treated with TBAF in chloroform, as shown in Scheme 2.15.

The mixture was stirred at room temperature for 24 hours, then assessed using ^{29}Si NMR. The ^{29}Si NMR spectrum in Figure 2.6 shows a group of peaks between -71 and -76 ppm and a set of septet at -187.23 ppm. This suggests that high molecular weight T-Si cage silsesquioxanes were produced together with some hexacoordinate $RSiF_6^{3-}$. In order to remove the TBAF, the mixture was extracted with water. However, after separation and removal of the solvent from the organic layer, the residue obtained did not dissolve in chloroform or other organic solvents. It seems that there was a reaction of the hexa-coordinate $RSiF_6^{3-}$ compound with water, giving rise to a reactive species that destroyed the silsesquioxane cages to give resins which did not dissolve in chloroform.



Scheme 2.15

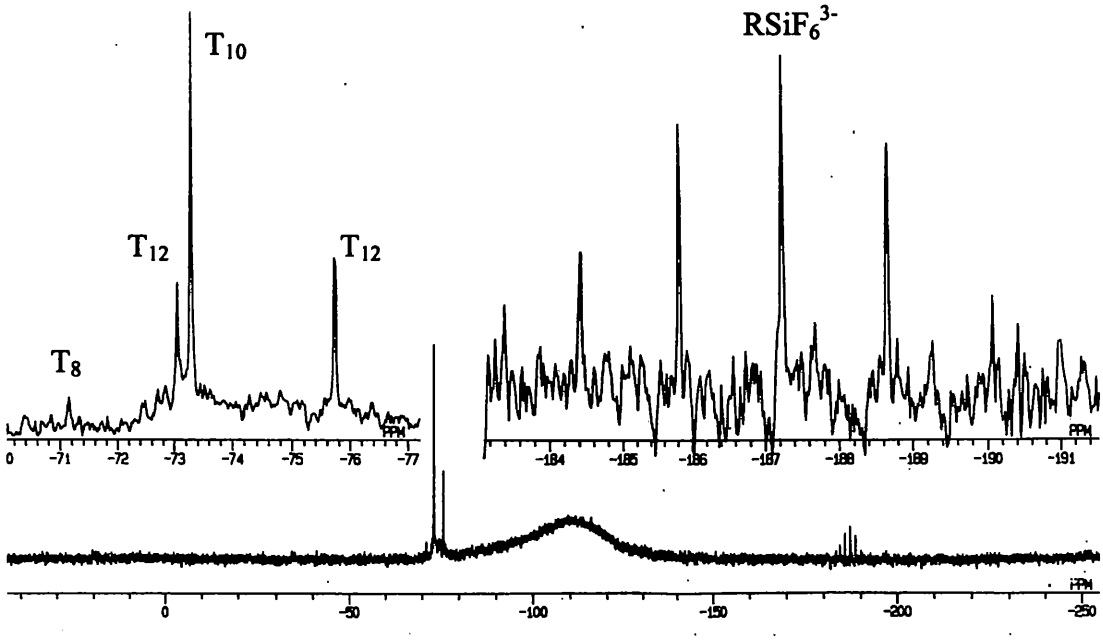


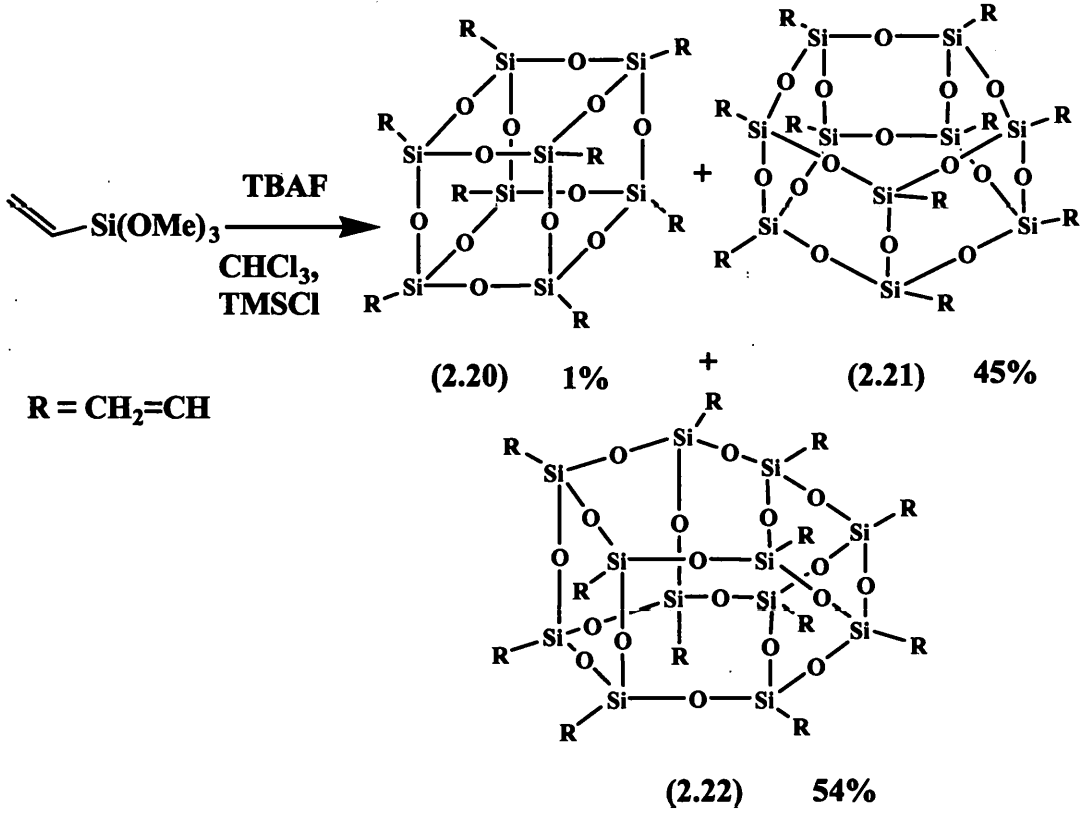
Figure 2.6

To avoid the generation of such active species after the cage had been formed, the reaction mixture was dried. Since the rearrangement of cyclopentyltriethoxysilane had demonstrated that some Si-O-Si frameworks containing silanol groups had been produced,

so the dried mixture was also silylated with TMSCl. Specifically, the reaction mixture was dried with 4 Å molecular sieve and then quenched with excess TMSCl for 4 hours. After removal of the molecular sieve, the volume of the solvent was reduced. On standing, a white solid precipitated out. Based on Marsmann's equations for the ^{29}Si NMR, it was clear that $AllylT_8$, $AllylT_{10}$ and $AllylT_{12}$ had been obtained in 3%, 76% and 21% yield respectively.

2.1.2.8 Reaction of vinyltrimethoxysilane

Bonhomme and co-workers reported[16] that octavinylsilsesquioxane was obtained from the hydrolysis of vinyltriethoxysilane using the strong acid, hydrochloric acid. Thus, vinyltrimethoxysilane was chosen because it was available in our laboratory and was treated with TBAF, as shown in Scheme 2.16.



Scheme 2.16

Vinyltrimethoxysilane was dissolved in chloroform followed by the addition of TBAF. The mixture was stirred at room temperature for 24 hours, after which a sample was examined

by NMR. A gel was obtained after removal of the solvent, but this gel did not dissolve in any common solvents, including chloroform. This suggests that the gel is a resin rather than well-defined silsesquioxane cages.

The reaction of vinyltrimethoxysilane with TBAF in chloroform was repeated again and stirring at room temperature for 24 hours. The reaction mixture was then treated as the same way as allytriethoxysilane. The reaction mixture was dried with 4Å molecular sieve and silylated with excess of TMSCl, followed by continued stirring for 4 hours. After filtration the solvent and the excess TMSCl were removed using a rotary evaporator at 30°C. A yellow solid gel was obtained which was extracted with a mixed solvent of hexane and chloroform to give a white solid. The ^{29}Si NMR spectrum of this solid is shown in Figure 2.7. Four peaks appear in the T_8-Si region at -80.19, -8133, -81.48 and -83.34 ppm indicating there are some high molecular weight silsesquioxanes produced. Although T_8R_8 cages usually appear at about -66 ppm, the chemical shift moves to a much high field when the silicon atoms are attached to an sp^2 carbon. The peak at -80.19 ppm is thought to arise from octavinylsilsesquioxane **2.20**,vinylT_8. Thus, based on the Marsmann's equation, the single peak at -81.48 ppm arises from decavinylsilsesquioxane **2.21**, vinylT_{10} and the peaks at -81.33 and -83.34 ppm from dodecavinylsilsesquioxanes **2.22**, vinylT_{12} cage with two different silicon environments. The yield of silsesquioxane cages is 1% vinylT_8, 45% vinylT_{10} and 54% vinylT_{12}. To confirm this speculation, the mixture was analysed by MALDI-TOF mass spectroscopy. The MALDI-TOF spectra are shown in Figure 2.8. The fragment at *m/z* 814.52 arises from the vinylT_{10} with a sodium ion and the peak at *m/z* 972.39 arises from the vinylT_{12} with a sodium ion. A small amount of vinylT_{14} at *m/z* 1130.39 was also observed, but there was little information on the vinylT_8 cage.

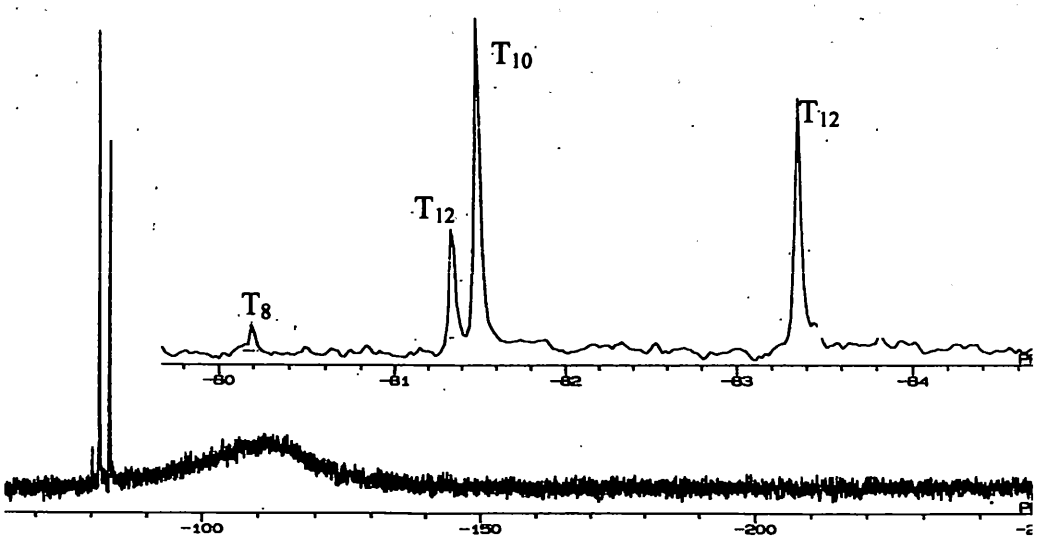


Figure 2.7

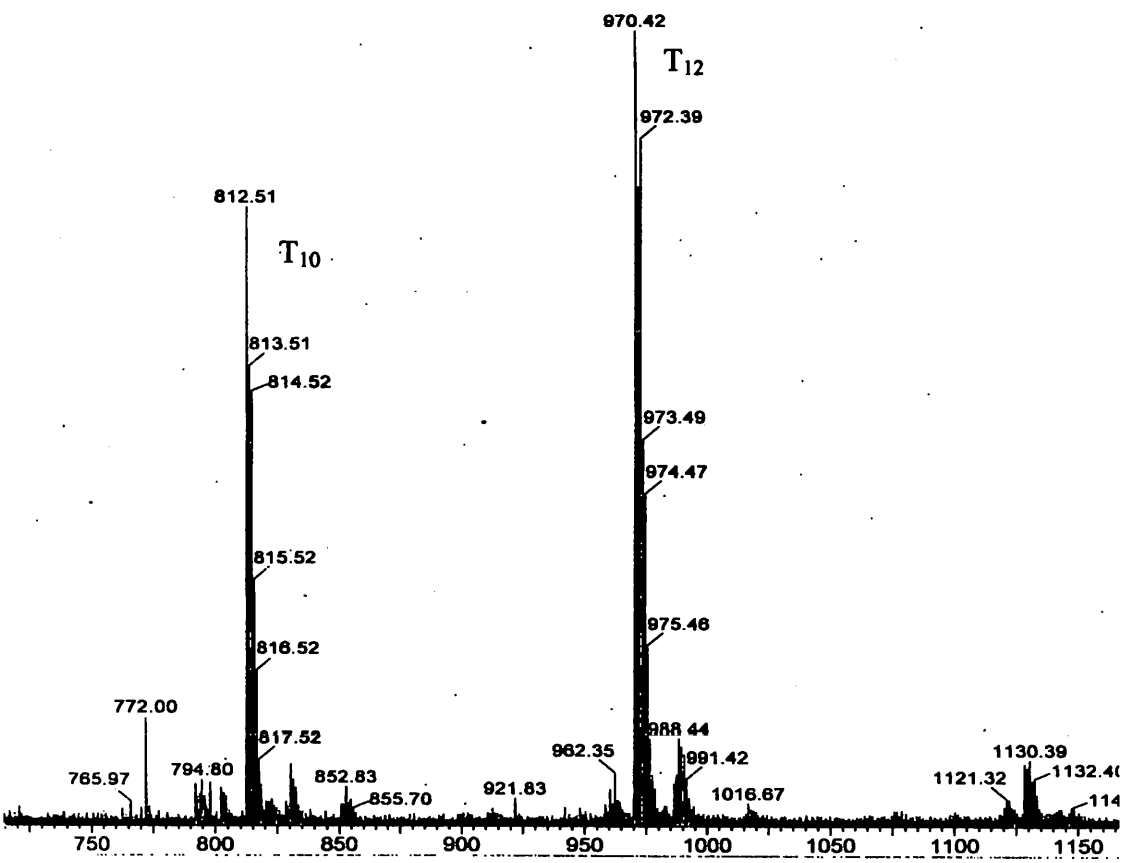
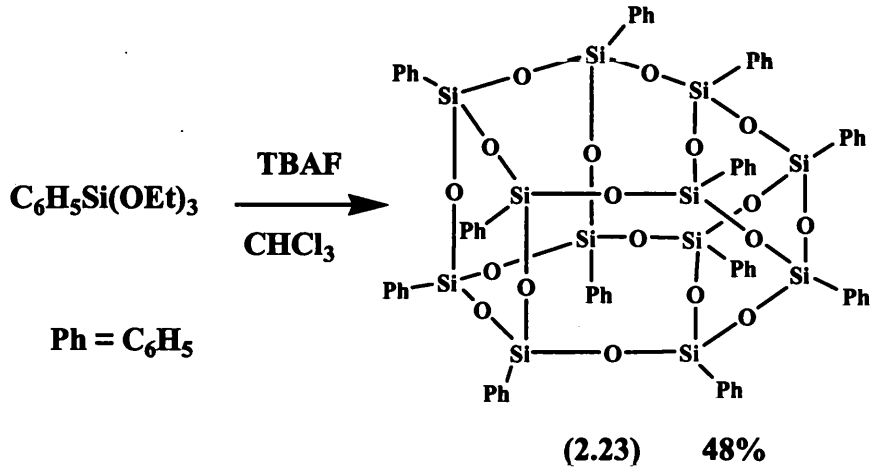


Figure 2.8

2.1.2.9 Reaction of phenyltriethoxysilane

As with vinyltrimethoxysilane, the silicon atoms are attached to an sp^2 carbon in phenyltriethoxysilane. Thus, the chemical shift of the phenylsilsesquioxanes would appear upfield of alkylsilsesquioxanes. The phenyl is also a relatively bulky group and octaphenylsilsesquioxane has been reported to be almost insoluble in all solvents.[17] So, octaphenylsilsesquioxane would readily precipitate out if the reaction were carried out in chloroform. Thus, phenyltriethoxysilane was treated with TBAF in chloroform as shown in Scheme 2.17.



(2.23) 48%

Scheme 2.17

The reaction mixture was stirred at room temperature for 24 hours during which some white solid precipitated out. The reaction mixture was filtered to give a white solid and the filtrate was stirred for another 24 hours. Filtration again gave a solid and the filtrate stirred for another 24 hours, which also gave a white solid after filtration. The solvent was then removed from this filtrate to give an oily residue. ^{29}Si NMR of the oily residue showed that, apart from two main peaks in the T-Si region at -69.69 and -79.87 ppm, there was a quintet at -125.17 ppm and a triplet at -187.64 ppm. However, ^{1}H NMR indicated that most of this residue was TBAF with only very small amount of phenyl containing compound. The quintet at -125.17 ppm in the ^{29}Si NMR was thought to be SiF_4, which is a gas at room temperature but can dissolved in some organic solvents, such as chloroform. However, this

should have been removed when the solvent was evaporated using a rotary evaporator at 40°C. Thus, this SiF_4 species is probably the pentacoordinate silicon compound, $PhSiF_4^-$, probably formed from the reaction of the phenytriethoxysilane with the fluoride. Another set of peaks at -187.64 ppm looks like a triplet, but the highfield chemical shift suggests they arise from $PhSiF_6^{3-}$ and the outer lines of the septet are lost in the noise. The peaks at -69.69 and -79.78 ppm in the T-Si region indicate that there was some cage framework formation. In order to confirm the identity of the components in the residue, it was analysed by MALDI-TOF mass spectroscopy, however no peaks were observed.

The white solid precipitated from the reaction mixture did not dissolved in common solvents, such as hexane, ether, dichloromethane, chloroform, acetone, methanol and water. The various solid samples were thought to be the same product so were collected together, and analysed by Magic Angle Spinning ^{29}Si NMR, as shown in Figure 2.9. Two peaks were observed at -76.82 ppm (with a shoulder peak at -77.48 ppm) and -80.40 ppm. This suggests that the solid is dodecaphenylsilsesquioxane **2.23**, PhT_{12}, with a yield of 48%. This speculation was confirmed by MALDI-TOF mass spectroscopy, which showed peaks at *m/z* 1573.02 ($M+Na^+$) and 1658.85 ($M+Ag^+$) corresponding to the PhT_{12} cage. This data indicated that the only silsesquioxane cage produced was PhT_{12}. The structure of the PhT_{12} cage consists of 4 Si-O four-membered rings and 4 Si-O five-membered rings giving two different silicon environments in the cage.

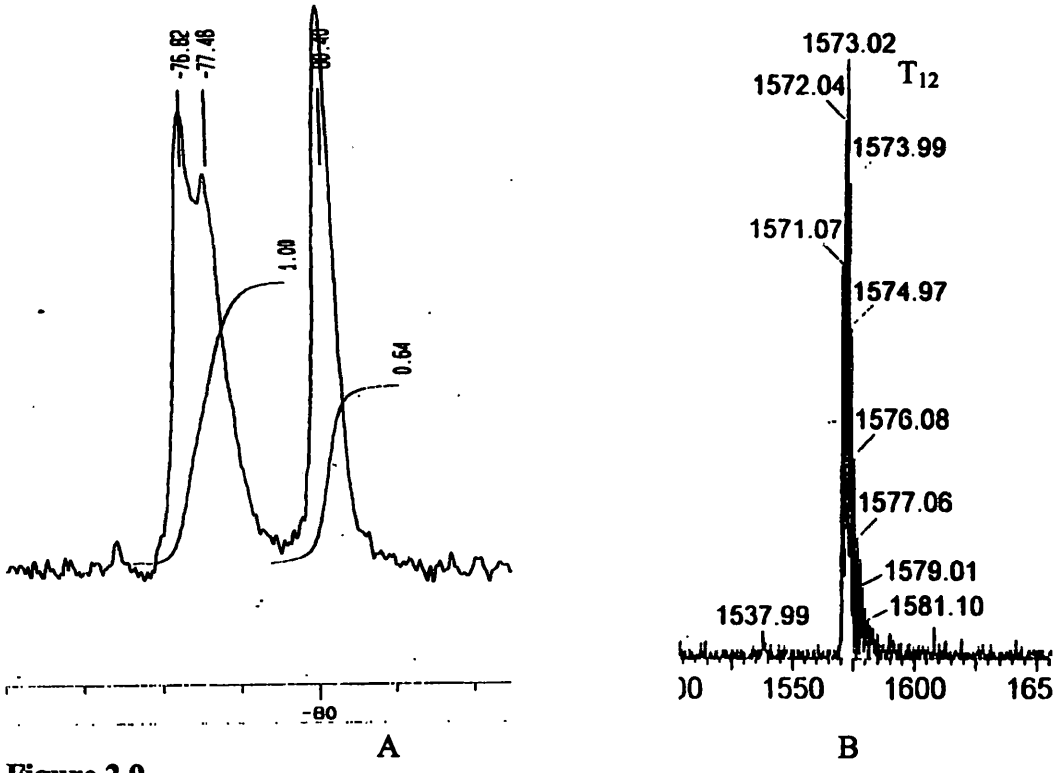


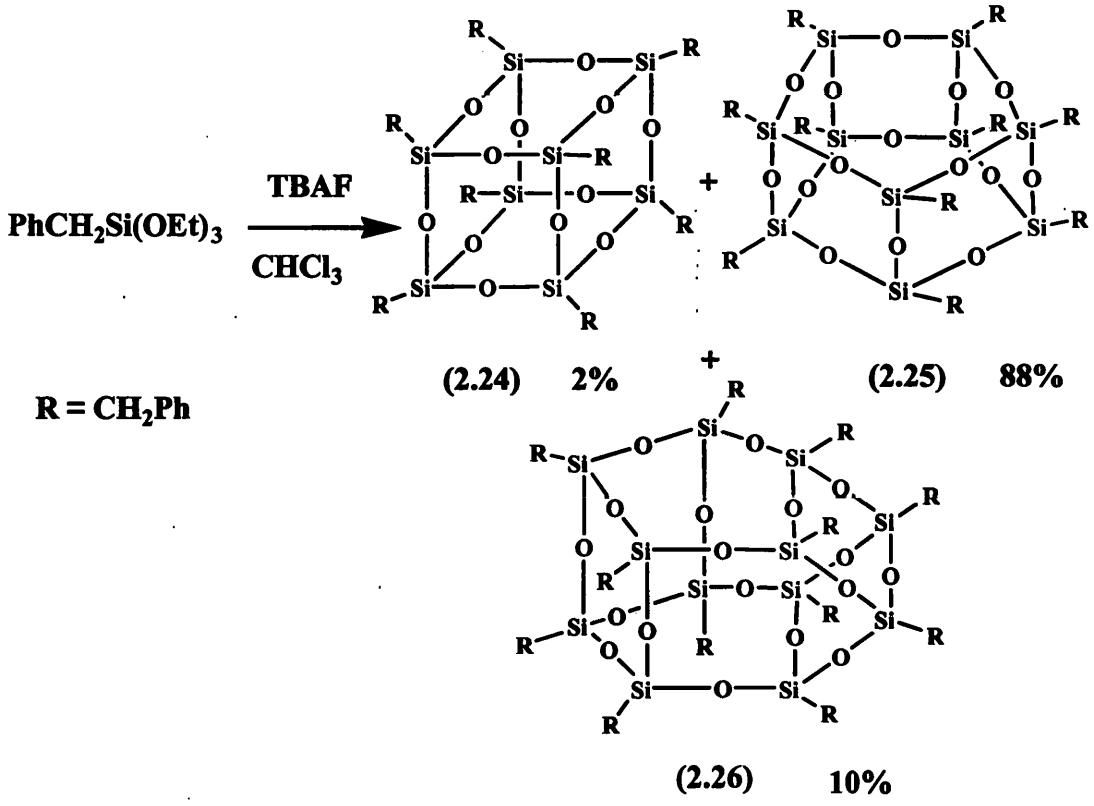
Figure 2.9

2.1.2.10 Reaction of benzyltriethoxysilane

In terms of the ^{29}Si NMR chemical shift, benzylsilsesquioxanes exhibit peaks at a lower field than phenylsilsesquioxanes. Although the octabenzylsilsesquioxane cage has been synthesised by Feher and co-workers, the preparation procedure is rather complicated involving hydrolytic condensation of benzyltrichlorosilane at high temperature.[8] Using our TBAF method, an octabenzylsilsesquioxane cage, BenzylT_8, would be produced readily in high yield. Therefore, benzyltriethoxysilane was treated with TBAF in chloroform, as shown in Scheme 2.18.

The reaction mixture of benzyltriethoxysilane with TBAF was stirred at room temperature for 24 hours. To stop the reaction and remove the TBAF, the mixture was extracted with water. After separation of the organic layer and removal of the solvent, a plain yellow gel was produced containing 88% BenzylT_{10} and 10% BenzylT_{12}, but there was only about 2% BenzylT_8 base on the NMR. BenzylT_{10} was the main product in this reaction, thus isolation of the BenzylT_{10} was attempted by recrystallisation, but it was not very successful.

Subsequent work within our research group has achieved the isolation of the BenzylT$_{10}$ by chromatography using a silica column.



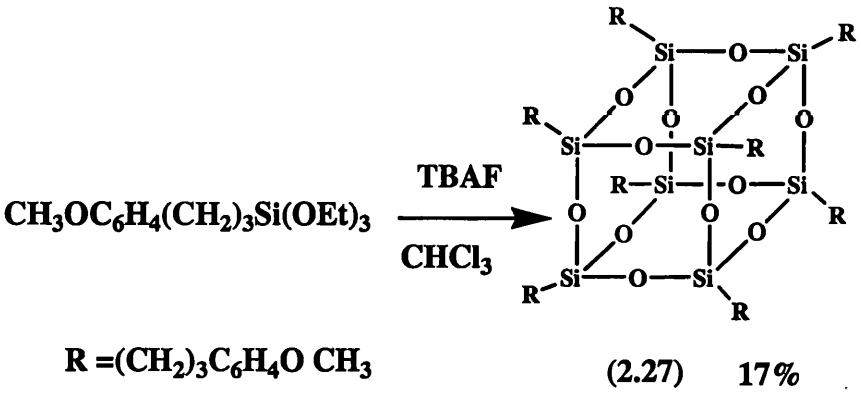
Scheme 2.18

2.1.2.11 Reaction of p-Methoxyphenylpropyltriethoxysilane

p-Methoxyphenylpropyl is another group containing a phenyl group, and the presence of a short chain enables them to pack efficiently such that the corresponding hexasilsesquioxane cage forms good crystals from hexane. Thus, reaction of *p*-methoxyphenylpropyltriethoxysilane with TBAF was carried out in chloroform, as shown in Scheme 2.19.

The reaction mixture was stirred at room temperature for 24 hours, then extracted with water to remove the TBAF. The organic layer was separated and a white solid gel residue was obtained after removal of the solvent. This residue was extracted with acetone to give a white solid product in 17.1% yield corresponding to the pure octa-*p*-methoxyphenyl-

propylsilsesquioxane, **2.27**, *p*-methoxyphenylpropylT_8 cage. The crystal structure of the *p*-methoxyphenylpropylT_8 cage was also obtained as discussed in Chapter 3.

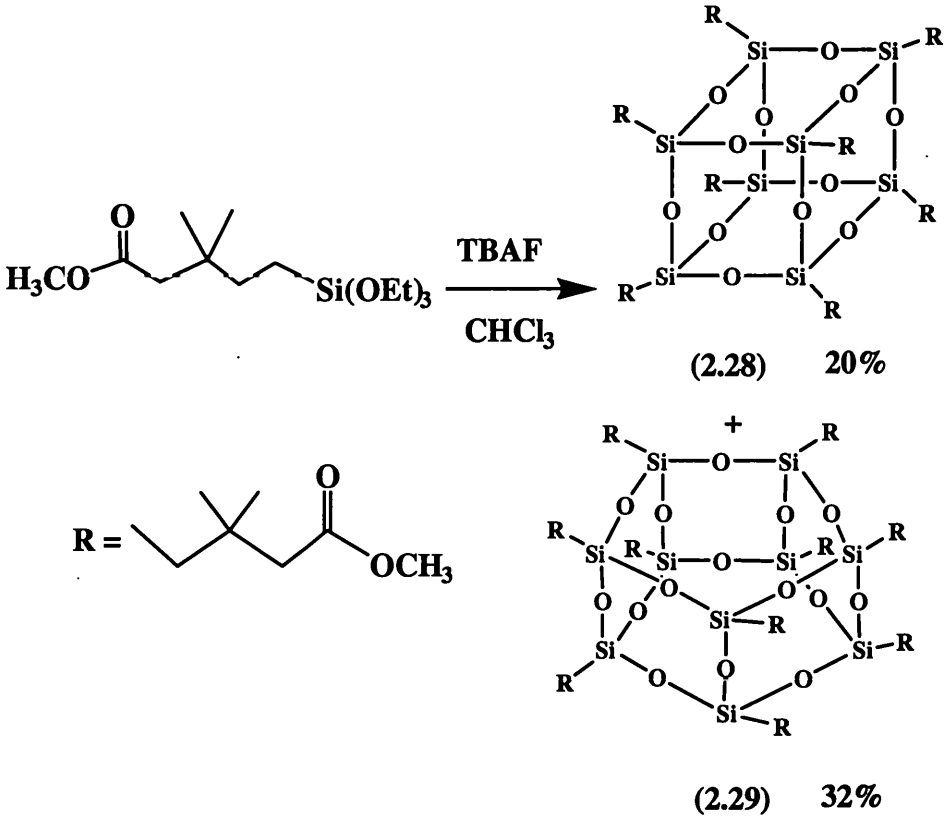


Scheme 2.19

2.1.2.12 Reaction of 5-methylcarboxy-3,3-dimethylpentyltriethoxysilane

The octasilsesquioxane of 5-methylcarboxy-3,3-dimethylpentane has been synthesised by hydosilylation of T_8H_8 with its alkene to give an ester functionalised unit that can be employed to make dendrimers and liquid crystals.[18,19] However the preparation is time consuming and the yields are relatively low. The previous work suggests that it should be possible to make octa-5-methylcarboxy-3,3-dimethylpentylsilsesquioxanes using our TBAF method. Thus, 5-methylcarboxy-3,3-dimethylpentyltriethoxysilane was treated with TBAF, as shown in Scheme 2.20.

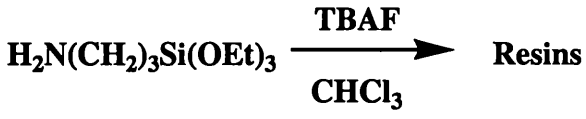
After 24 hours stirring at room temperature, the reaction mixture was extracted with water. A yellow oily gel was obtained after removal of the solvent from the organic layer. The ^{29}Si NMR suggested high molecular weight octasilsesquioxane and decasilsesquioxane cages were obtained and gave 20% T_8 **2.28** and 32% T_{10} **2.29** along with some unreacted starting material.



Scheme 2.20

2.1.2.13 Reaction of 3-aminopropyltriethoxysilane

To expand the diversity of functional silsesquioxanes, 3-aminopropyltriethoxysilane was treated with TBAF, as shown in Scheme 2.21.



Scheme 2.21

The reaction was performed in chloroform by stirring the reaction mixture at room temperature. After 30 minutes a great deal of white solid precipitated out from the mixture. The white solid was filtered off and the filtrate continued stirring. The white solid had a poor solubility in chloroform. ^{29}Si NMR gave no information on the nature of the products except that only one peak appeared at -39.36 ppm corresponding to the starting material. The powder was washed with chloroform to give a white solid which had a very low melting temperature. Unfortunately, this solid did not dissolve in any solvent, so NMR

could not be used for characterisation. Feher and co-workers have reported[18] that aminosilsesquioxanes are unstable after removal of solvent, and that the amino functionalised silsesquioxane may only be stable under acid conditions. Thus the product probably decomposed after filtration of the reaction mixture.

2.1.2.14 Reaction of 3-mercaptopropyltriethoxysilane

To expand the diversity of functional silsesquioxanes further, 3-mercaptopropyltrimethoxysilane was treated with TBAF in chloroform, as shown in Scheme 2.22. The reaction was carried out as before, but unfortunately, it gave a resin with a very poor solubility rather than a well-defined silsesquioxane.

$$HS(CH_2)_3Si(OEt)_3 \xrightarrow[CHCl_3]{TBAF} \text{Resins}$$

Scheme 2.22

2.1.3 Summary of the reaction of alkyltriethoxysilanes with TBAF

Alkyltriethoxysilanes are T units that can be used to build up high molecular weight silsesquioxane cages in good yield by the reaction with TBAF. In particular, octasilsesquioxane cages with cyclopentyl and cyclohexyl groups attached to the core were obtained in up to 94.8% yield in a one-pot reaction. Based on the formation of silsesquioxanes, the reactivity of alkyltriethoxysilanes is,

Methyl >Vinyl > Allyl > hexyl > octyl > *iso*-butyl > cyclopentyl > cyclohexyl

Table 2.4 summarises that the yield of octasilsesquioxanes obtained from the corresponding trialkoxysilanes. With bulky groups such as cyclopentyl and cyclohexyl, the octasilsesquioxane is readily obtained as a stable species using TBAF. By contrast, the smaller groups such as methyl lead to a resin, and the less bulky groups give not only octasilsesquioxanes but also higher molecular weight silsesquioxane cages, such as $T_{10}R_{10}$ and $T_{12}R_{12}$. With Phenyl group, only dodecaphenylsilsesquioxane, PhT_{12}, was produced in

high yield. The reaction has subsequently been shown to be solvent dependent, such that in different solvent systems, the octaphenylsilsesquioxane cage could be obtained. More remarkably, recent work on this system has revealed that an octaphenylsilsesquioxane cage with a fluoride ion trapped in the centre of the cage can be prepared by this method.

We believe that TBAF is an excellent catalyst for the condensation reaction of silsesquioxanes. TheTBAF rearrangement of other silsesquioxane systems, such as octasilsesquioxanes and hexasilsesquioxanes will be discussed in detail later in this and the next chapter.

Table 2.4 Yield of Silsesquioxanes from the Corresponding Triethoxysilane

$RSi(OEt)_3$, R=	Solvent	Time (hour)	Yield (%)		
			T_8	T_{10}	T_{12}
c-C_5H_9	Acetone	4	94.8	–	–
c-C_6H_{11}	Acetone	4	83.6	–	–
$(CH_3)_2CHCH_2$	Chloroform	24	14.7	–	–
*$CH_3(CH_2)_7$	Chloroform	24	58	26	–
*$CH_3(CH_2)_5$	Chloroform	24	50	21	–
CH_3	Chloroform	24	–	–	–
*CH_2=$CHCH_2$	Chloroform	24	3	76	21
*CH_2=CH	Chloroform	24	1	46	53
C_6H_5	Chloroform	3 × 24	–	–	48
*$C_6H_5CH_2$	Chloroform	24	2	88	10
P-$CH_3OC_6H_4(CH_2)_3$	Chloroform	24	17.1	–	–
*$CH_3OCO(CH_2)_2C(CH_3)_3CH_2$	Chloroform	24	20	32	–
$H_2N(CH_2)_3$	Chloroform	24	–	–	–
$HS(CH_2)_3$	Chloroform	24	–	–	–

* The yield was calculated by ^{29}Si NMR.

2.2 Rearrangement of Octasilsesquioxane Cages

The initial stages of this part of the work focussed on the degradation of octasilsesquioxane cages. Feher and co-workers reported [20]that one Si-O-Si linkage in an octacyclohexylsilsesquioxane could be cleaved to give a partial opened cage silsesquioxane using HBF_4/BF_3. The reaction was repeated to ensure that the reaction conditions were applicable to other octasilsesquioxanes. Marsmann and co-workers have also demonstrated[3] that octasilsesquioxanes could be rearranged using bases to give high molecular weight cages such as deca and dodecasilsesequioxane, i.e. $T_{10}R_{10}$ and $T_{12}R_{12}$, using bases, such as potassium carbonate, sodium hydroxide, sodium acetate and sodium sulphite. However the details of the experimental and quantitative work were not extensive. In this work, the rearrangement reactions of other octasilsesquioxanes were examined using similar reagents and followed using HPLC to analyse the reaction mixture. Furthermore, it had been demonstrated in the previous section that TBAF could be used to form well-defined high molecular weight silsesquioxane cages. Thus, it appears a possibility that octasilsesquioxanes could be rearranged by TBAF to give higher molecular weight silsesquioxane cages, such as $T_{10}R_{10}$ and $T_{12}R_{12}$. Again, Marsmann's equation for the chemical shifts of the ^{29}Si NMR of the cages is very useful for the identification of the reaction mixture.

In this section we will discuss the use of TBAF as a catalyst for the rearrangement reaction of octasilsesquioxane cages. Oxygen nucleophiles together with a range of electrophiles were also employed to study the rearrangement of the octasilsesquioxane cage T_8R_8, in order to understand the mechanism of redistribution of silsesquioxane cages.

2.2.1 Synthesis of Octasilsesquioxanes

The rearrangement of the following octasilsesquioxanes, T_8R_8, were examined, where R = cyclohexyl, heptyl, octyl, nonyl, decyl, dodecyl and phenoxypentyl. The main reason for

choosing this series was that the corresponding T_8R_8 compounds were well characterised and the synthetic expertise was available in our research group. In particular, the octasilsesquioxane with a 5-phenoxypentyl group on the core would be very useful for HPLC analysis because it contains phenyl chromophore groups , which could be easily detected using an UV detector.

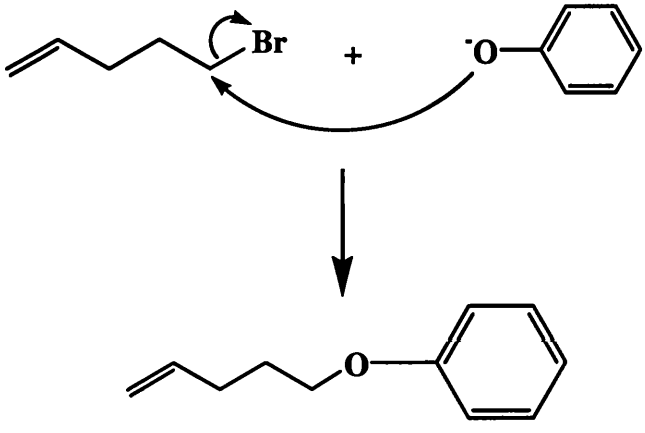
2.2.1.1 Synthesis of Octacyclohexylsilsesquioxane

Octacyclohexylsilsesquioxane could be synthesised in high yield by reaction of the cyclohexyltriethoxysilane with TBAF in acetone.

2.2.1.2 Synthesis of Octaalkylsilsesquioxane

Octaalkylsilsesquioxanes, T_8R_8, with a linear carbon chain attached to the core, were synthesised in a traditional way by hydrosilylation of T_8H_8 with alkenes and a platinum catalyst. Although we have demonstrated that alkyltriethoxysilanes could give octa, deca and dodecasilsesquioxanes in high yield, by reaction with TBAF, the isolation of the pure T_8R_8 was not straightforward.

The alkenes such as 1-heptene, 1-octene, 1-nonene, 1-decene, and 1-dodecene are commercially available, but not phenoxy-1-pentene. This was prepared using a Williamson synthesis as shown in Scheme 2.23.

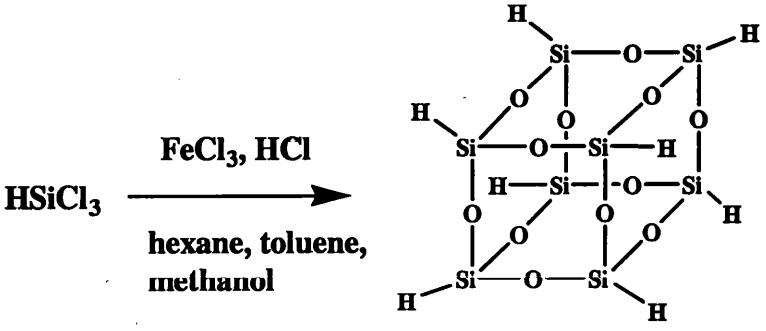


(2.30) **31%**

Scheme 2.23

A solution of 5-bromo-1-pentene in dry acetone was refluxed with phenol for 3 days with excess potassium carbonate to give the product **2.30** in 31.4% yield.

T_8H_8 **2.31** was synthesised by hydrolytic condensation of trichlorosilane as shown in Scheme 2.24, based on a refinement of the trichlorosilane hydrolysis route,[7,9] which in turn was a refinement of the method of Frye and co-workers.[6]

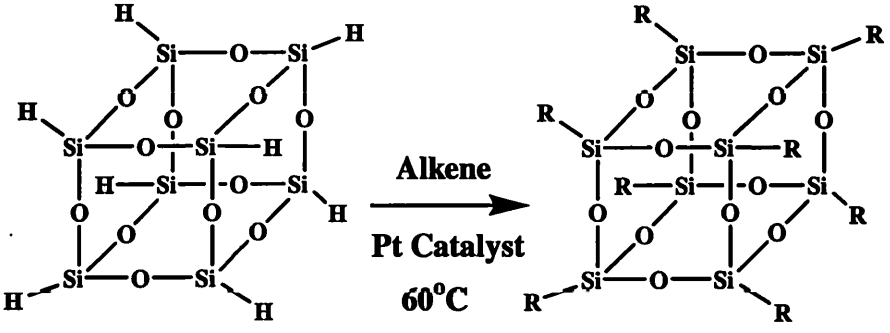


(2.31)

Scheme 2.24

Recrystallization of the crude product is necessary, because there are small amounts of decahydrosilsesquioxane, $T_{10}H_{10}$ and dodecahydrosilsesquioxane, $T_{12}H_{12}$, formed as well. T_8H_8 was obtained at 7.3% yield after recrystallization from hot hexane.

The next stage involves attachment of the arms to the cage by hydrosilylation. This was carried out in high yield using the method of Bassindale and co-workers.[9] T_8H_8 was hydrosilylated with alkenes using a platinum catalyst as shown in Scheme 2.25.



Scheme 2.25

The T_8H_8 and the various alkenes were mixed in a small vial containing the platinum catalyst. This mixture was heated to 60°C and the reaction followed by IR, which showed the reaction to be completed on the disappearance of the Si-H peak at 2156 cm^{-1}. The NMR showed that only the β-addition product was formed in agreement with other such hydrosilylations of terminal alkenes. In general, the product obtained by this route is of sufficient purity to be used without further purification. However, sometimes it was necessary to purify the sample further by column chromatography on silica gel using toluene as the eluent to remove the platinum catalyst. The purity was checked using ^{1}H, ^{13}C and ^{29}Si NMR. The ^{29}Si NMR spectra showed a single peak at about -66 ppm. The yield of octaalkylsilsesquioxanes from hydrosilylation is summarised in Table 2.5.

Table 2.5 The yield of octasilsesquioxanes from hydrosilylation

Alkene	Product	Yield (%)
1-Heptene	Octaheptylsilsesquioxanes (**2.32**)	78.5
1-Octene	Octaoctylsilsesquioxane (**2.33**)	89.8
1-Nonene	Octanonylsilsesquioxane (**2.34**)	72.4
1-Decene	Octadecylsilsesquioxane (**2.35**)	86.4
1-Dodecene	Octadodecylsilsesquioxane (**2.36**)	83.6
Phenoxy-1-pentene	Octa-5-phenoxypentylsilsesquioxane (**2.37**)	97.4

2.2.2 Rearrangement of Octasilsesquioxanes

2.2.2.1 Using an electrophilic reagent

Two kinds of electrophiles HBF_4/BF_3[20] and triflic acid, TfOH,[21] were used. Although Feher and co-workers have performed this reaction with octacyclohexylsilsesquioxane, to give the cage product arising from cleavage of one Si-O-Si linkage, other

octasilsesquioxane cages, with alkyl groups on the core have not been investigated.

OctylT_8, was chosen because it is an exemplar of the silsesquioxanes with a linear alkyl group on the core and is easy to prepare by hydrolsilylation of T_8H_8, with 1-octene.

a) Reaction of octaoctylsilsesquioxanes with mixture of HBF_4 and BF_3

The OctylT_8 was treated with a mixture of $HBF_4{\cdot}OMe_2$ and $BF_3{\cdot}OEt_2$. In order to study this reaction in more detail and understand more about the process of cleavage of Si-O-Si linkages, the reaction was monitored using ^{29}Si NMR. The NMR spectra were collected each hour for a period of 16 hours. As shown in Figure 2.10, the Si-O-Si linkage of the OctylT_8 was cleaved after one hour to form a partial cage. The amount of the partial T_8 cage increased at the expense of the starting material, OctylT_8. Thus the reaction was repeated on a preparative scale by refluxing for 2.5 hours and then allowing to cool down to room temperature. The reaction mixture was analysed by ^{29}Si NMR, which gave the spectrum in Figure 2.11 showing that only one partial cage product **2.38** was produced with some unreacted starting materials and that only one Si-O-Si linkage in the OctylT_8 was cleaved. Attempts to isolate the open cage were not successful because the physical state of octaoctylsilsesquioxane with a linear carbon chain on the core is a wax, so that fractional recrystallization is not possible. Also the opened cage difluoro compound would stick to the column, so chromatography was also unsuccessful.

In order to examine the difluoro opened cage compound, the reaction mixture was left at room temperature for a longer time (a few days). The reaction remains at about 70% (by NMR) conversion because the cleavage of Si-O-Si linkage becomes no longer favourable since the water produced leads to dilution of the $HBF_4{\cdot}OMe_2$ and $BF_3{\cdot}OEt_2$.

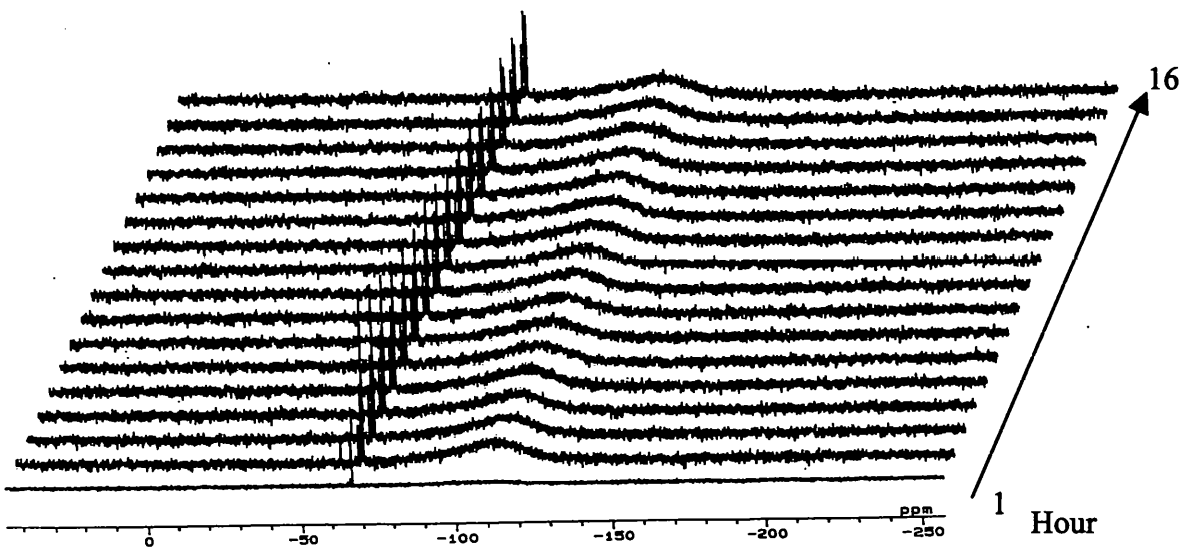


Figure 2.10

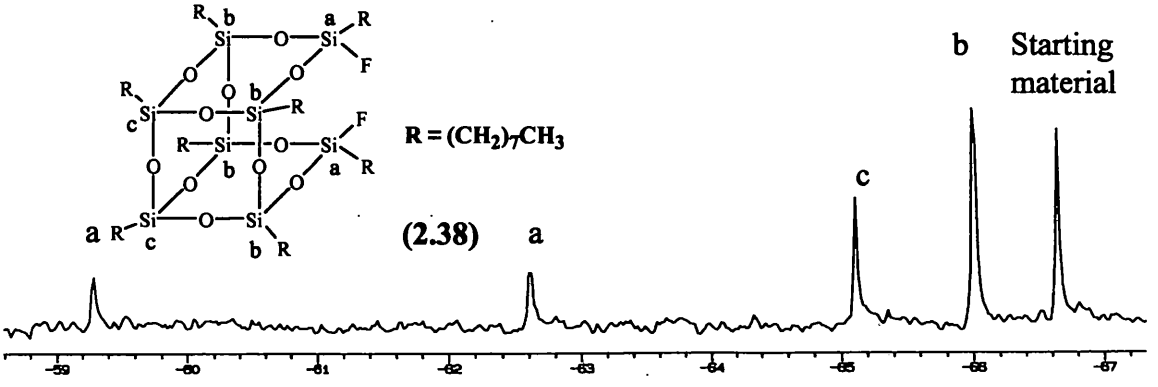
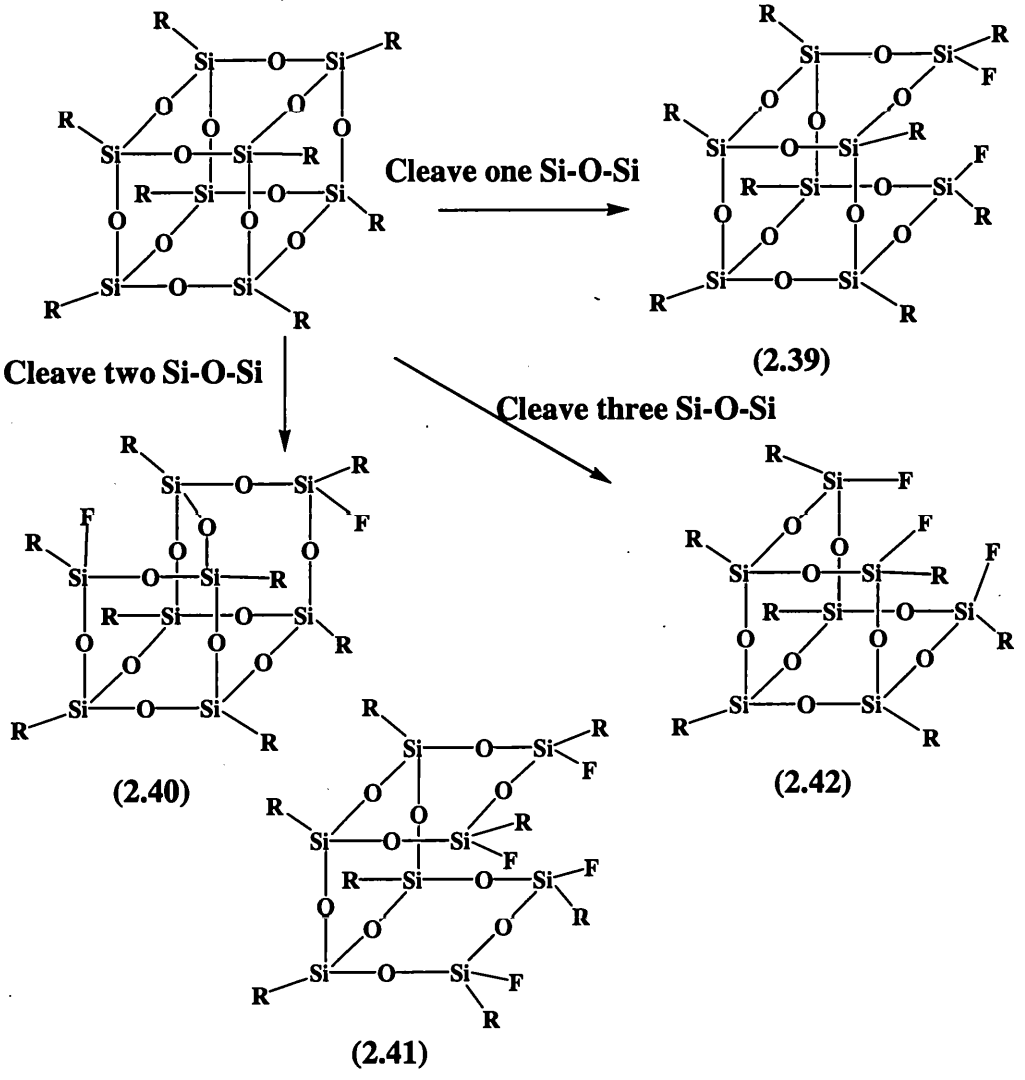


Figure 2.11

Repeating the reaction with twice amount of $HBF_4{\cdot}OMe_2$ and $BF_3{\cdot}OEt_2$, and then leaving it to react overnight resulted in the reaction mixture separating into two layers. Separation of these two layers followed by removal of the solvent gave a brown residue from the lower layer and a white oily wax from the upper layer. The brown residue had no signals in the ^{29}Si NMR, although the ^{1}H and ^{13}C NMR show the presence of water and $HBF_4{\cdot}OMe_2$ and $BF_3{\cdot}OEt_2$ species. The ^{29}Si NMR of the white oily wax from the upper layer is shown in Figure 2.12. The spectra show that the OctylT$_8$ has been completely reacted. The coupling constant of a Si-F linkage is about 260 Hz suggesting there are four partial cages formed and other unknown products. One, two and three Si-O-Si linkages in the OctylT$_8$ could be

cleaved to give a difluoride coompound **2.39**, tetrafluoride compounds **2.40**, **2.41** and trifluoride compound **2.42**, as shown in Scheme 2.26.



Scheme 2.26

When only one Si-O-Si linkage was cleaved in the OctylT_8 cage, there was only one partial cage **2.39** formed, which would appear as three peaks in a ratio of 2:2:4. When two Si-O-Si linkages were cleaved, two compounds, **2.40**, **2.41** would be produced. These two isomers would give different patterns of peaks in the ^{29}Si NMR.**2.40** would have four peaks in a ratio of 2:2:2:2 and **2.41** would have only 2 peaks in a ratio of 4:4. If three Si-O-Si linkages of OctylT_8 were cleaved, an open corner partial cage OctylT_7F_3 **2.42** would be formed, which would has three peaks in a ratio of 3:1:3. Of course, the Si-F bond of these compounds would appear as a doublet in the ^{29}Si NMR.

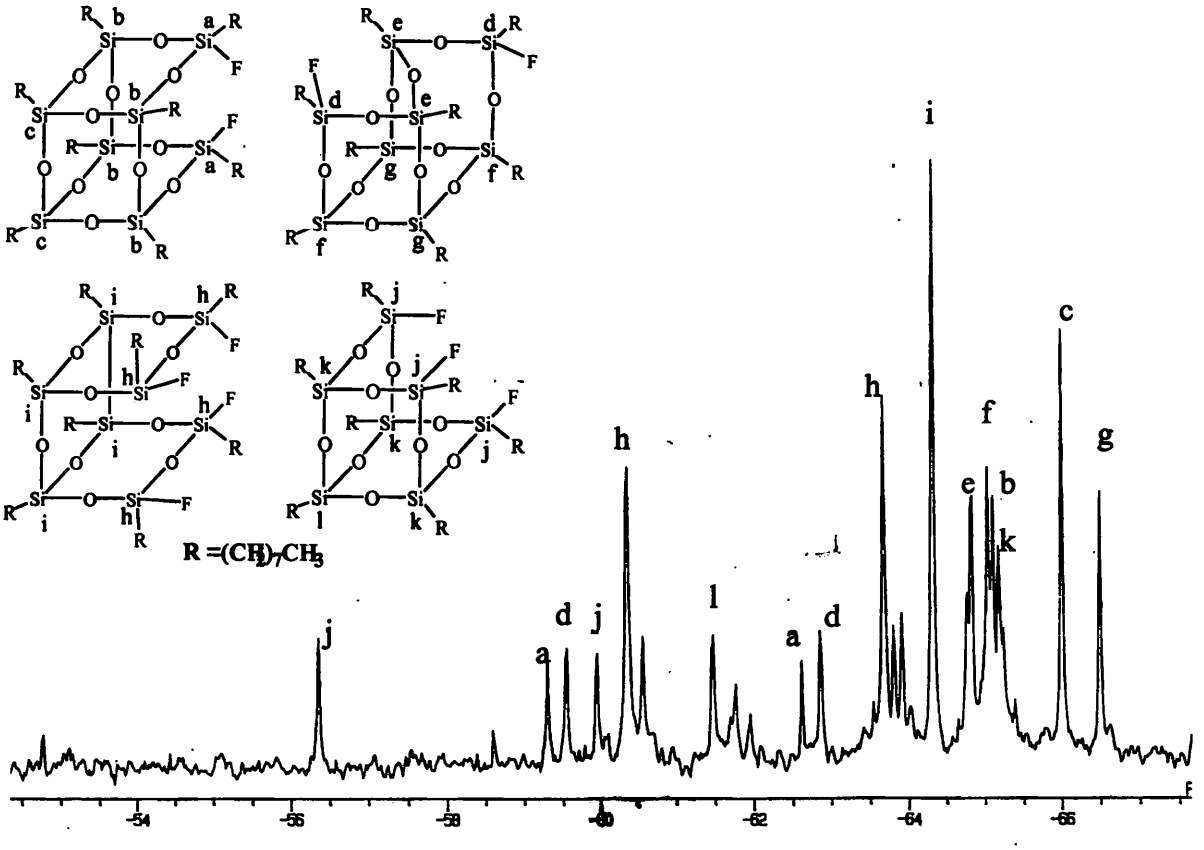


Figure 2.12

b) Using triflic acid

Octyl T_8 was treated with triflic acid, TfOH, and then the reaction mixture analysed by ^{29}Si NMR, which showed that the Si-O-Si linkages of OctylT_8 were cleaved to give some partial Si-O-Si frameworks. However, the spectra were too complex to identify the components.

2.2.2.2 Using oxygen nucleophiles

Marsmann and co-workers have reported[3] that octasilsesquioxanes, T_8R_8, could be rearranged to higher molecular weight compounds, such as $T_{10}R_{10}$ and $T_{12}R_{12}$, in the presence of basic catalysts. They also demonstrated that the product mixture could be analysed by normal phase HPLC and NMR. However, the procedure for the analytical techniques was not given in great detail. Thus, rearrangement of octa-5-phenoxypentylsilsesquioxane, 5-phenoxypentylT_8, was studied using a similar strategy to Marsmann. 5-phenoxypentylT_8 was refluxed with a base in dry acetone. The bases used were sodium acetate, potassium carbonate, sodium

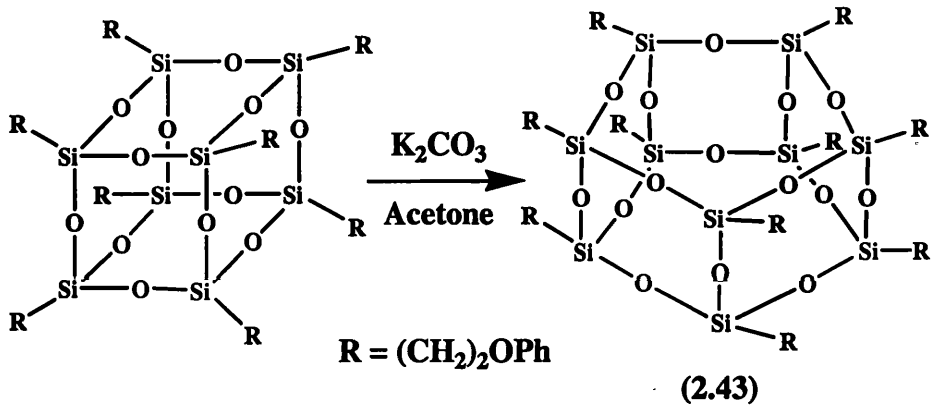
hydroxide and sodium trimethylsilanolate. The reaction mixtures were analysed by HPLC, NMR and Mass spectroscopy.

a) Rearrangement using sodium acetate

Octa-5-phenoxypentylsilsesquioxane, 5-phenoxypentylT_8, was treated with sodium acetate. After 24 hours reflux in acetone and removal of the solvent, the reaction mixture was analysed by NMR and HPLC using 1-chlorobutane as eluent. Only one peak with a retention time at 22.83 minutes appeared in the HPLC chromatogram, which indicated that there was no reaction between the 5-phenoxypentylT_8 cage and sodium acetate. The ^{29}Si NMR also showed the presence of only the starting material, 5-phenoxypentylT_8, with a single peak at -66.74 ppm.This illustrated that sodium acetate was not a strong enough base or nucleophile to cleave the Si-O-Si linkage in the 5-phenoxypentylT_8 cage.

b) Rearrangement using potassium carbonate

Potassium carbonate is a stronger base than sodium acetate. The previous reaction had shown that there was no degradation or rearrangement of the 5-phenoxypentylT_8 cages with sodium acetate. Thus, 5-phenoxypentylT_8 was treated with potassium carbonate. After 24 hours the solvent was removed, and the reaction residue analysed by NMR and HPLC using 1-chlorbutane as eluent. The HPLC chromatogram, showed two peaks with retention times of 18.52 and 22.87 minutes. The peak at 18.52 minutes corresponds to starting material, 5-phenoxypentylT_8 (The temperature of column was increased so that the retention time of 5-phenoxypentylT_8 was shorter than before.). Thus, the peak at 22.87 minutes must be due to a new product. However, it was not possible to identify this product based solely on this result.



(2.43)

Scheme 2.27

The ^{29}Si NMR showed two peaks at -66.65 and -68.52 ppm. Based on Marsmann's equations, the peak at -68.52 ppm is probably due to the decasilsesquioxane cage **2.43**, 5-phenoxypentylT_{10}. If the rearrangement reaction is reversible, it is not surprising that a mixture of 5-phenoxypentylT_8 and 5-phenoxypentylT_{10} was obtained (Scheme 2.27). In order to confirm the presence of 5-phenoxypentylT_{10}, other analytical methods will need to be used. In particular, preparative HPLC would be very useful to obtain a pure sample of the rearranged product. However, our attempts were not very successful because of the limitations of the preparative scale HPLC equipment in our laboratory.

c) Rearrangement using sodium hydroxide

Octa-5-phenoxypentylsilsesquioxane, 5-phenoxypentylT_8, was also treated with sodium hydroxide which is a stronger base. However, analysis of the reaction product by ^{29}Si NMR and HPLC gave little insight into the outcomes. There was only one peak in the HPLC chromatogram and the ^{29}Si NMR spectrum. Marsmann and co-workers have suggested that the catalyst needs to be chosen to match the silsesquioxane. For 5-phenoxypentylT_8, sodium hydroxide may not be a suitable catalyst for this rearrangement reaction.

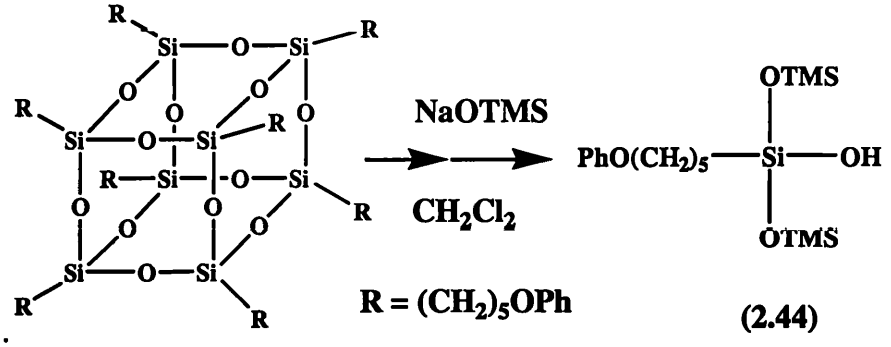
d) Rearrangement using sodium trimethylsilanolate

Since the catalyst has to be chosen to match the silsesquioxanes, sodium trimethylsilanolate was used because it is less basic. Sodium trimethylsilanolate is commercially available in a solution of dichloromethane. Thus the reaction of octa-5-phenoxypentylsilsesquioxane, 5-phenoxypentylT_8, with sodium trimethylsilanolate was performed in dry dichloromethane. The mixture was refluxed for 24 hours. The reaction was stopped and after removal of the solvent gave a colourless residue. This residue was analysed by ^{29}Si NMR. Since the catalyst, sodium trimethylsilanolate, is sensitive to moisture, some of the peaks in the spectrum correspond to the catalyst and its hydrolytic by-products. The ^{29}Si NMR of the product mixture exhibits three peaks at 8.59, -55.77 and -66.72 ppm. The peak at -66.72 ppm corresponds to unreacted starting material, 5-phenoxypentylT_8 and the peak at 8.59 ppm arises from sodium trimethylsilanolate. The peak at -55.77 ppm indicated that a new product has been produced whose chemical shift is located in the T-Si region corresponding to a silanol group. In order to simplify the ^{29}Si NMR spectra of the product, the catalyst was removed from the reaction mixture by washing with saturated sodium bicarbonate solution. The organic layer was separated from the aqueous layer, and after removal of the solvent gave an oily product. The residue was dissolved in deuterated dichloromethane for NMR analysis. The ^{29}Si NMR spectrum was not very different to the original sample, only the ratio of the peaks had changed. The most probable structure that gives rise to the chemical shift at -55.77 ppm is 5-phenoxypentyl-dimethylsiloxy silanol **2.44**. The reaction mixture was further analysed using HPLC with an Evaporative Light Scattering Detector (ELSD) with 1-chlorbutane and chloroform (3:1) as eluent. The retention time of the peaks is shown in the Table 2.6.

Table 2.6 ELSD-HPLC analysis of the rearrangement reaction mixture of 5-phenoxypentylT_8 using sodium trimethylsilanolate

Peaks	Retention time	Components
Peak1	4.77	Starting material
Peak2	11.48	Product
Peak3	12.77	Product

The peak at 4.77 min corresponds to the starting material and the other compounds came out after the starting material at 11.48 min and 12.77 min. This information suggests that a degradation reaction of the 5-phenoxypentylT_8 cage occurred in basic conditions. It was possible that the peak at 12 min corresponded to the 5-phenoxypentyldimethylsiloxy silanol **2.44**, because the OH group makes it more polar than the starting material. However, there is not enough information to speculate on how the starting material is redistributed to give the lower molecular weight compound. The identity of the other oligomer in the reaction mixture may provide important information for identifying the mechanism and thus mass spectroscopy was employed. However, due to the limitation of the instrument, no information on the high molecular weight compounds could be obtained. Significantly a peak at *m/z* 384 was observed which corresponded to the structure of **2.44**.



The identification of only unreacted starting material and low molecular weight monosilyl **2.44** suggested that the initial cleavage of the cage is the rate-limiting step and once this has occurred, subsequent break-down of oligomers was very rapid.

HPLC with an UV detector was also employed to analyse the reaction mixture of the rearrangement reaction of 5-phenoxypentylT_8 using sodium trimethylsilanolate. Table 2.7 showed the retention time of components in the mixture. These results suggested that preparative column HPLC may be employed to separate the mixture, however, so far this has proved difficult.

Table 2.7 UV-HPLC analysis of the rearrangement reaction mixture of 5-phenoxypentylT_8 using sodium trimethylsilanolate

Peaks	Retention time	components
Peak1	4.75	Starting material
Peak2	17.74	Product

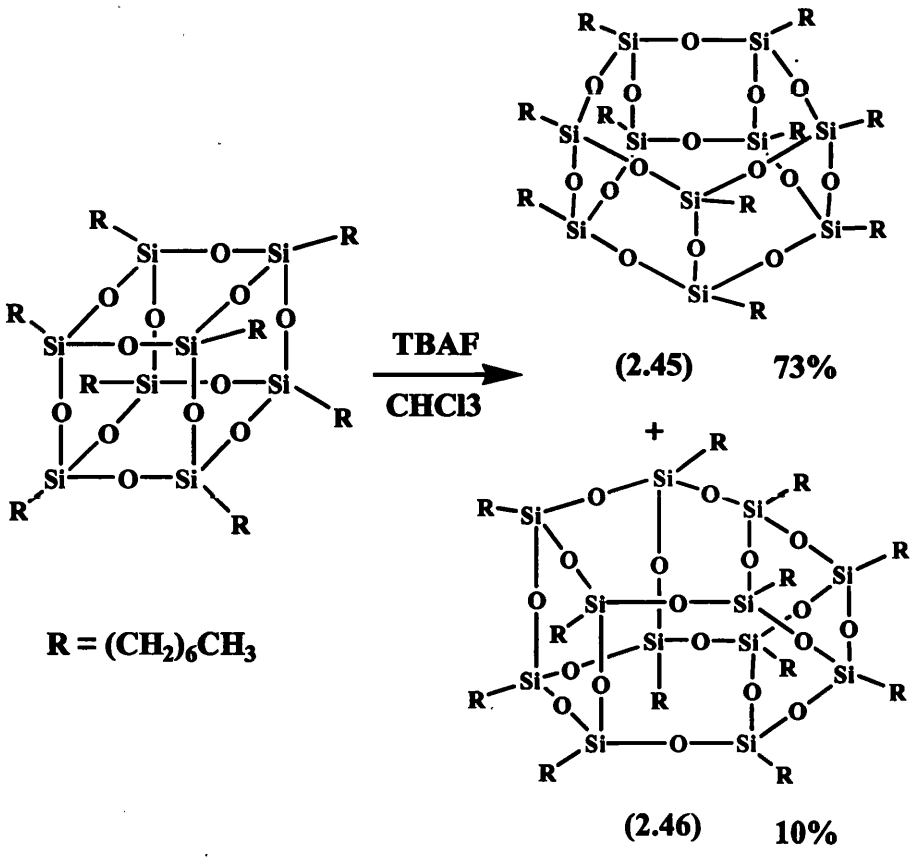
2.2.2.3 Rearrangement using tetra-n-butylammonium fluoride solution

a) Rearrangement of octaheptylsilsesquioxane

Octaheptylsilsesquioxane, HeptylT_8, has been well characterised, and Marsmann and co-workers have demonstrated[3] that HeptylT_8 can be rearranged to decasilsesquioxane cages, HeptylT_{10}, but no dodecasilsesquioxane, HeptylT_{12} was obtained. Thus, HeptylT_8 was treated with TBAF in chloroform as shown in Scheme 2.28.

The ^{29}Si NMR spectrum of the product is shown in Figure 2.13 exhibiting a group of peaks between -65 and -71 ppm. It is obvious that the main product has peaks at -68.38, -68.55 and -70.82 ppm with some starting material appearing at -66.64 ppm. Using Marsmann's equation, the calculated values for the ^{29}Si NMR chemical shift are -68.38 ppm for HeptylT_{10} **2.45** and -68.31 and -70.91 ppm for HeptylT_{12} **2.46**, which has two silicon

environments. The distribution of heptylsilsesquioxanes produced after overnight reaction with TBAF was 73% HeptylT_{10} and 10% HeptylT_{12} with 16% starting material, HeptylT_8



Scheme 2.28

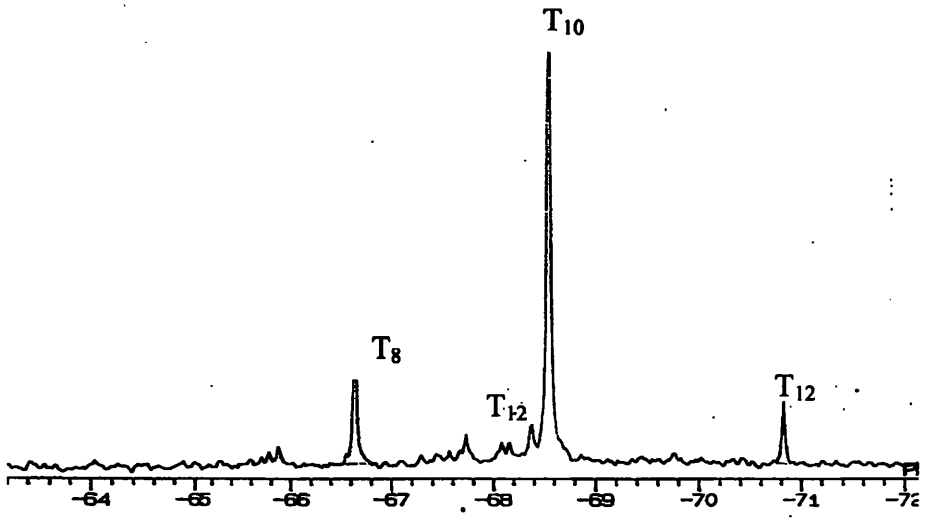
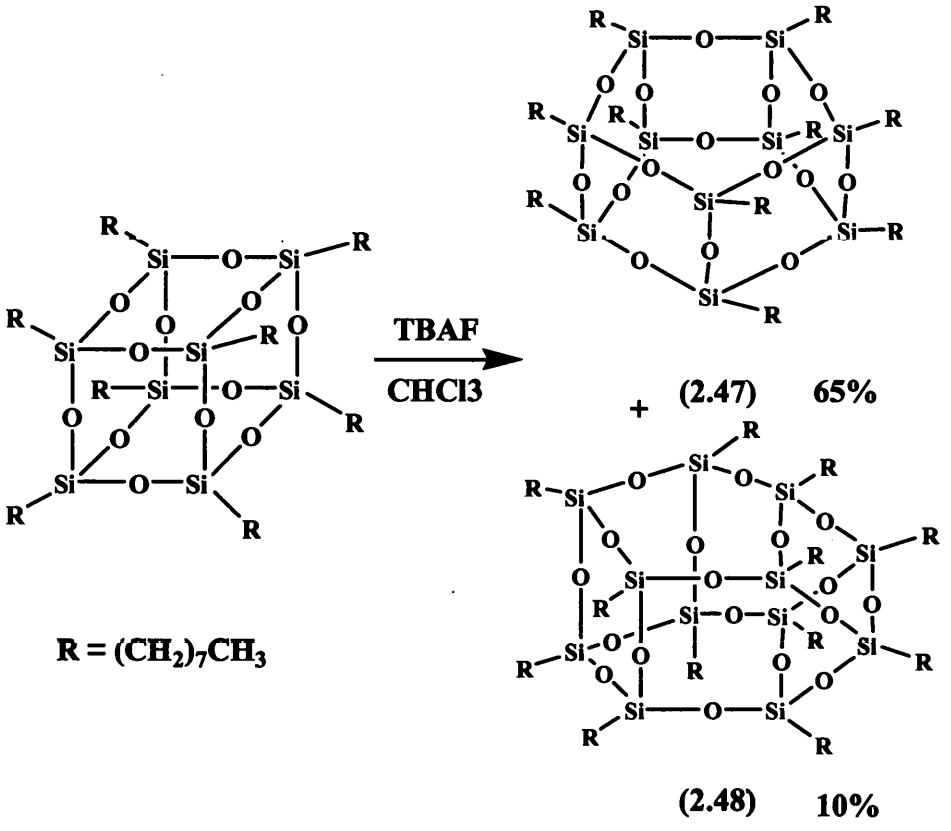


Figure 2.13

b) Rearrangement of octaoctylsilsesquioxane

As the same reason, octaoctylsilsesquioxane, OctylT_8, has been rearranged to the higher molecular weight cage decaoctylsilsesquioxane, OctylT_{10} (15%) using potassium carbonate, but no dodecasilsesquioxane, OctylT_{12}, was formed under these conditions. Thus the OctylT_8 was chosen for the rearrangement reaction with TBAF, Scheme 2.29.



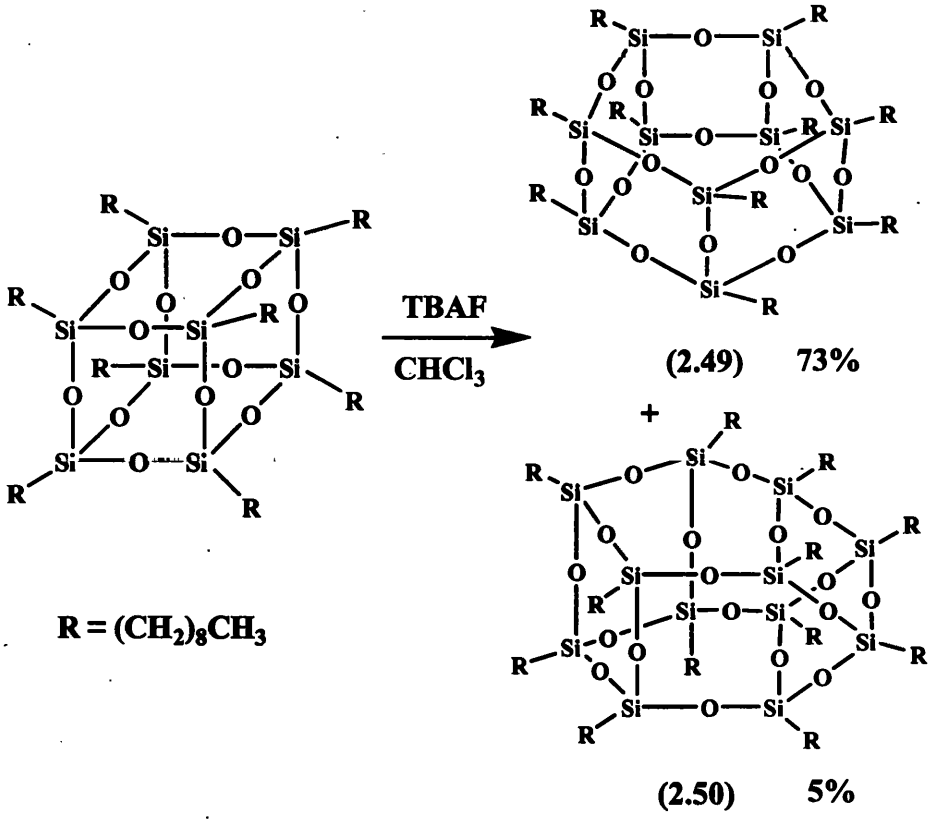
Scheme 2.29

OctylT_8 was treated with TBAF in chloroform and the reaction mixture stirred at room temperature overnight. ^{29}Si NMR showed that OctylT_{10} **2.47** and OctylT_{12} **2.48** was produced with some starting material based on the calculation of chemical shift using the Marsmann's equations. Based on the NMR, there was about 65% OctylT_{10} and 10% OctylT_{12} along with 24% starting material OctylT_8.

c) Rearrangement of octanonylsilsesquioxane

As with octaoctylsilsesquioxane, OctylT_8, octanonylsilsesquioxane, NonylT_8, was rearranged to decanonylsilsesquioxane, NonylT_{10}, (8%) using potassium carbonate and

dodecasilsesquioxane, NonylT$_{12}$, was not formed in the reaction. Therefore, nonylT$_8$ was treated with TBAF in chloroform, as shown in Scheme 2.30. The reaction mixture was stirred at room temperature overnight, then the reaction mixture was analysed by ^{29}Si NMR. However, ^{29}Si NMR showed little evidence of any other silsesquioxanes except the starting material. Thus the reaction mixture was stirred for another day. The reaction mixture was then extracted with water and the organic layer separated. After removal of the solvent, a white oily gel was obtained. The ^{29}Si NMR of this gel showed 73% NonylT$_{10}$ and 5% NonylT$_{12}$ was produced with 15% NonylT$_8$ remaining.

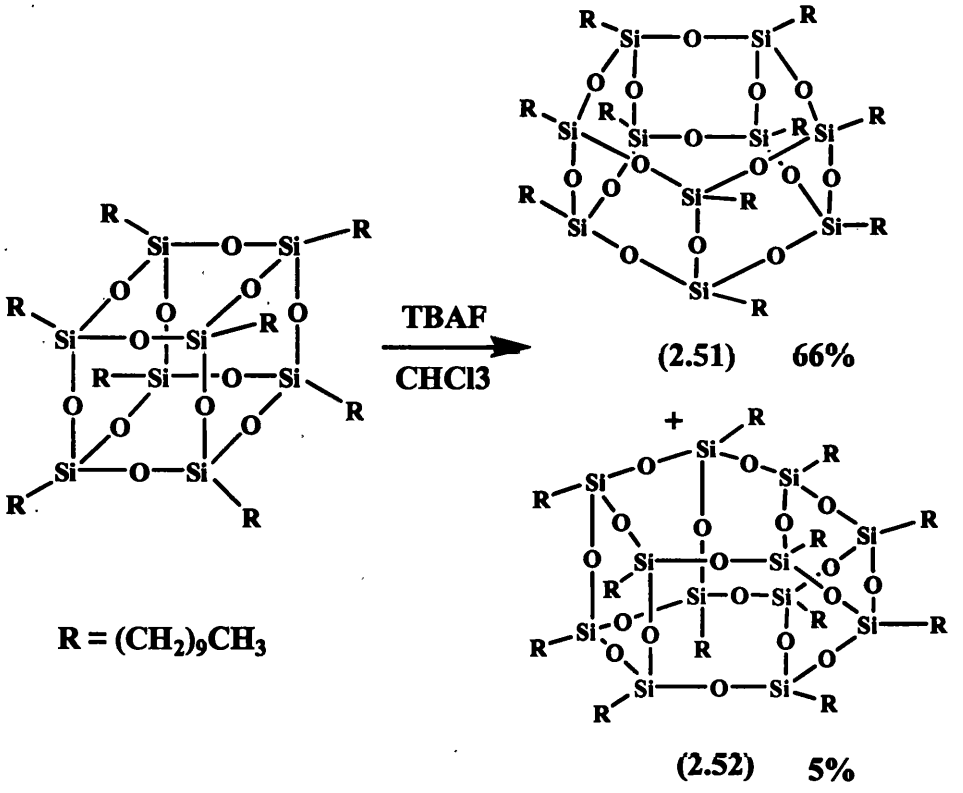


Scheme 2.30

d) Rearrangement of octadecylsilsesquioxane

Octadecylsilsesquioxane, DecylT$_8$, was treated with TBAF as before. However, the reaction mixture was left for a longer time, as shown in Scheme 2.31. After one and half days stirring, the reaction mixture was extracted with water to give an oily product. The ^{29}Si NMR exhibited four major peaks at -66.91, -68.70, -68.82 and -71.10 ppm. The peak at -66.91 ppm confirms there is still some starting material remaining. The major peak at

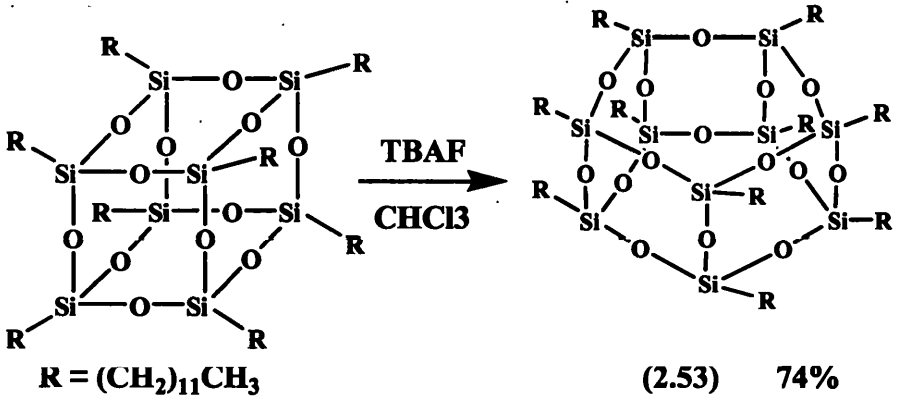
-68.82 ppm indicates the formation of decadecylsilsesquioxane **2.51**, DecylT_{10}. The peaks at -68.70 and -71.10 ppm with ratio of 1:2 are evidence of dodecadecylsilsesquioxane **2.52**, DecylT_{12}. Based on the NMR, DecyT_{10} was obtained in 66% yield and DecylT_{12} was produced in 5% yield with 18% DecyT_8 remaining.



Scheme 2.31

e) Rearrangement of octadodecylsilsesquioxane

Octadodecylsilsesquioxane, DodecylT_8, was treated with TBAF at room temperature, as shown in Scheme 2.32.



Scheme 2.32

After one and half days, the reaction was analysed by ^{29}Si NMR. However, ^{29}Si NMR showed no other silsesquioxanes except starting material. Thus, the reaction was stirred for a further 2 days after, there was still plenty of starting material, but with a small peak at -68.92 ppm appeared in the ^{29}Si NMR. Therefore, the reaction mixture was stirred for another 2 days, then extracted with water to give an oily gel product. ^{29}Si NMR showed there are two peaks at -66.98 and -68.92 ppm, indicating that the DodecylT_8 was partially rearranged to decadodecylsilsesquioxanes, DodecylT_{10}. The distribution of silsesquioxane cages is 26% DodecylT_8 and 74% DodecylT_{10} with no evidence for the formation of dodecadodecylsilsesquioxane, DodecylT_{12}.

In summary, ^{29}Si NMR shows that on treatment with TBAF, octasilsesquioxane cages, T_8R_8, were rearranged to decasilsesquioxane cages, $T_{10}R_8$, and dodecasilsesquioxane cages, $T_{12}R_{12}$, although some starting material did remain. The ^{29}Si NMR is very diagnostic for these cages and Marsmann's equations have been extremely useful in characterisation of the larger cages.

Table 2.8 compares the chemical shift of the T_8R_8, $T_{10}R_{10}$ and $T_{12}R_{12}$ observed in the ^{29}Si NMR spectra together with the theoretical chemical shift values calculated using Marsmann's equations.

These data indicate that the experimental value and the theoretical value are very close. The NMR spectrum of the product obtained from rearrangement of the DodecylT_8 cage shows no DodecylT_{12}. This indicates that the rearrangement of DodecylT_8 with TBAF was much slower than other alkylT_8. One explanation is that since the dodecyl group has the longest carbon chain in the series of heptyl, octyl, nonyl, and decyl, it will be more difficult to be opened using TBAF, so that the rearrangement would be effectively slower. Therefore, reaction of dodecylT_8 with TBAF was continued for a further 5 days, and analysed by ^{29}Si NMR. The spectrum still showed the presence of some starting material, DodecylT_8 and a single peak for DodecylT_{10} with no evidence of DodecylT_{12} formation.

Table 2.8 Comparison of chemical shift from calculated value and observed value

R	δT_8	δT_{10}		δT_{12A}		δT_{12B}	
	Obs.	*Cal.	*Obs.	Cal.	Obs.	Cal.	Obs.
C_7H_{15}	-66.64	-68.51	-68.55	-68.31	-68.38	-70.91	-70.82
C_8H_{17}	-66.63	-69.27	-69.36	-69.07	-69.05	-71.70	-71.62
C_9H_{19}	-66.63	-68.51	-68.57	-68.31	-68.11	-70.91	-70.84
$C_{10}H_{21}$	-66.91	-68.67	-68.82	-68.58	-68.70	-71.19	-71.10
$C_{12}H_{23}$	-66.98	-68.86	-68.92	---	---	---	---

*Cal - calculated chemical shift, Obs - Observed chemical shift.

The comparison of all the spectra data suggests the amount of $T_{12}R_{12}$ cage decreased with increasing the length of the carbon chain. It also indicates that the reactivity of these cages with TBAF decreases with the increasing the length of the carbon chain and the order is,

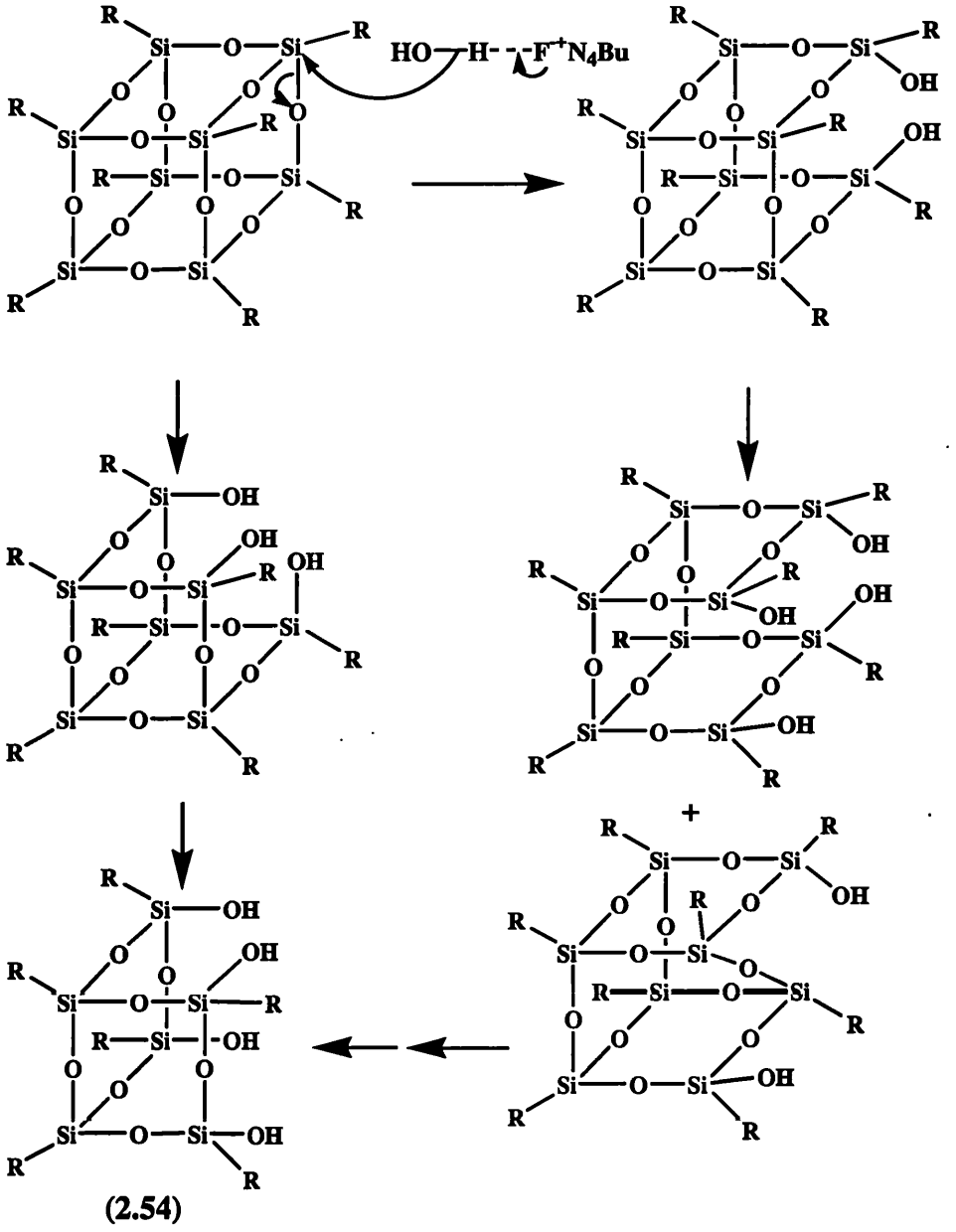
Heptyl >Octyl >Nonyl >Decyl >Dodecyl

The distribution of T_8R_8, $T_{10}R_{10}$ and $T_{12}R_{12}$ obtained using TBAF is shown in the Table 2.9.

Table 2.9 Distribution of Silsesquioxanes (based on ^{29}Si NMR)

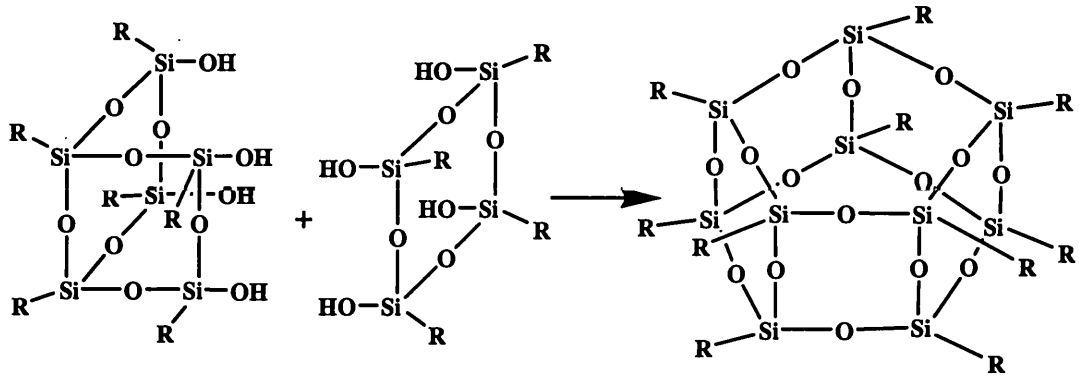
$R_8Si_8O_{12}$, R=	Time (day)	Yield (% in NMR)		
		T_8R_8	$T_{10}R_{10}$	$T_{12}R_{12}$
C_7H_{15}	0.5	16	73	10
C_8H_{17}	0.5	24	65	10
C_9H_{19}	1.5	15	73	5
$C_{10}H_{21}$	1.5	18	66	5
$C_{12}H_{23}$	5.5	26	74	_

From these experimental observations, the mechanism of the these rearrangement reactions can be proposed that the Si-O-Si linkages of the octasilsesquioxane cages was cleaved at the first stage, as shown in Scheme 2.43. The silicon atom is attacked by a nucleophile to cleave one, two or three Si-O-Si linkages of the cage. The partial cages are carried on the cleavage of Si-O-Si in the further steps, and a tetrol **2.54** is produced. A soon as the tetrol was formed, this tetrol is condensed in two ways to give the higher molecular weight cages thermodynamically, either decasilsesquioxane or dodecasilsesquioxane cages, as shown in Scheme 2.44 and Scheme 2.45. More details of the cleavage of these Si-O-Si linkages will be discussed in Chapter 3.

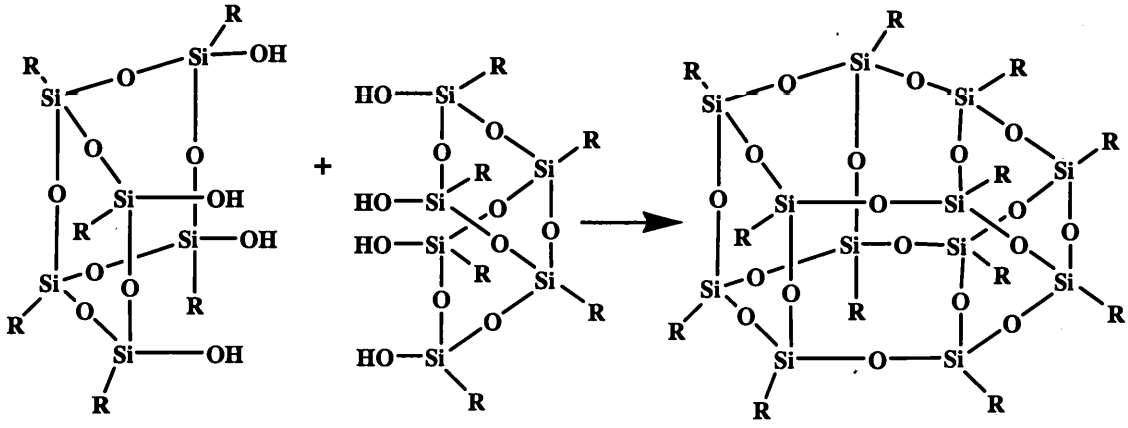


(2.54)

Scheme 2.33



Scheme 2.34

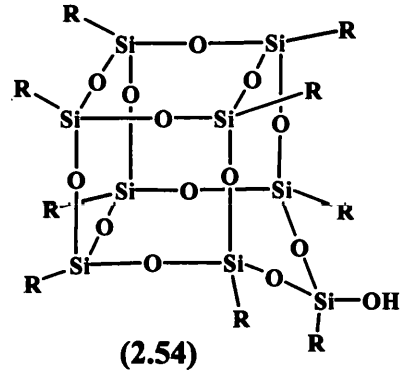


Scheme 2.35

f) Rearrangement of octacyclohexylsilsesquioxane

Octacyclohexylsilsesquioxane, CyT_8, is different from the other octaalkylsilsesquioxanes in that it has a bulky cyclohexyl group on the core compared to the other linear alkyl groups. CyT_8 has been well characterised[8] and it has been degraded to give a partial cage. Thus, CyT_8 was treated with TBAF (excess) solution. The reaction mixture was stirred at room temperature and followed by ^{29}Si NMR. After 24 hours, there was still a single peak at -68.99 ppm due to the starting material. Thus, the reaction mixture was refluxed for one hour. However, there was still no change in the ^{29}Si NMR. The reaction mixture was then refluxed for 24 hours. The ^{29}Si NMR is shown in Figure 2.14 and exhibits a group of peaks between -59 to -72 ppm and a quintet at -115.91 ppm with the main peak arising from the

starting material, CyT_8. This indicated that CyT_8 with cyclohexyl groups on the core was rearranged only partially to other silsesquioxanes and that some $RSiF_4^-$ was also produced. The mixture was refluxed for a further 24 hours. The ^{29}Si NMR showed little change, the main peak at -69.23 ppm arising from CyT_8. The small peaks being between -68 to -72 ppm were found to be due to a silsesquioxane cage **2.54**, CyT_9OH, which will be discussed in more detail in the next chapter.



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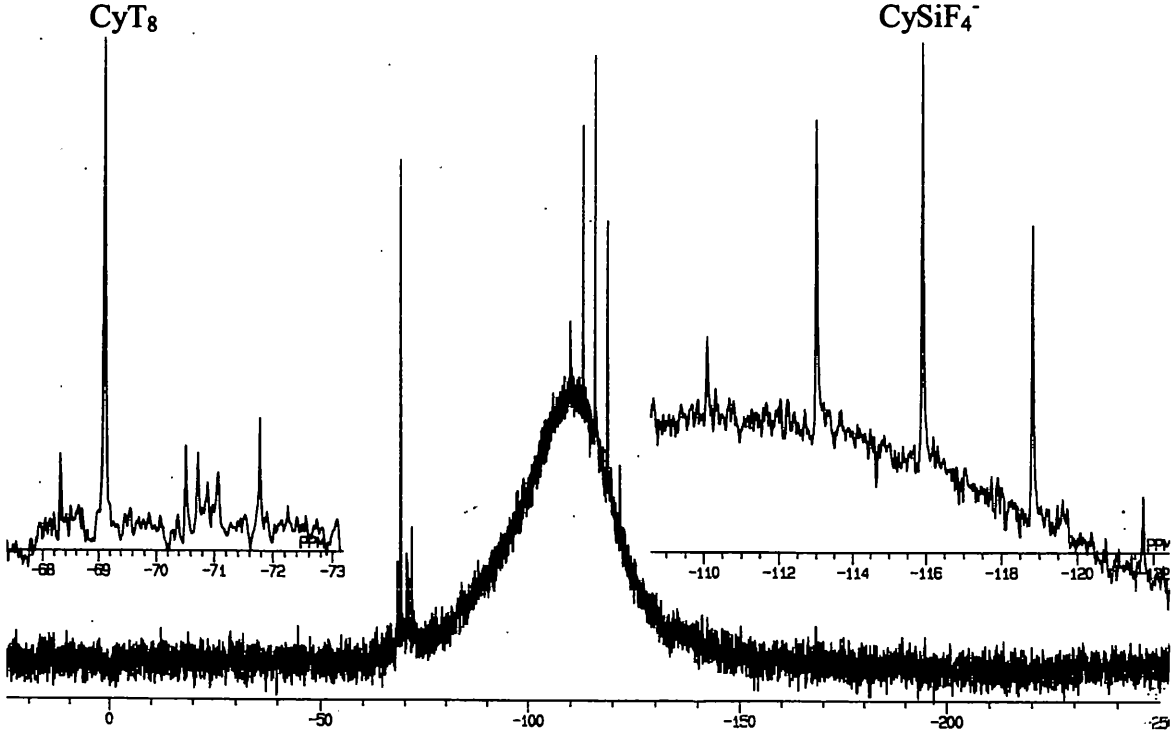


Figure 2.14

g) Rearrangement of octahydrosilsesquioxane

Octa and decahydrogensilsesquioxane, T_8H_8, and $T_{10}H_{10}$, could be synthesised by hydrolytic condensation of trichlorosilane, but the yield of the product is very low and a large amount of organic solvent is required. Since octaalkylsilsesquioxanes rearrange to high molecular weight cages, $T_{10}R_{10}$ and $T_{12}R_{12}$, this provides an opportunity to exploit our methodology to produce $T_{10}H_{10}$ cages from T_8H_8 cages. If this rearrangement proves successful, there is great potential to elaborate these cages by exploiting the Si-H groups in hydrosilylation.

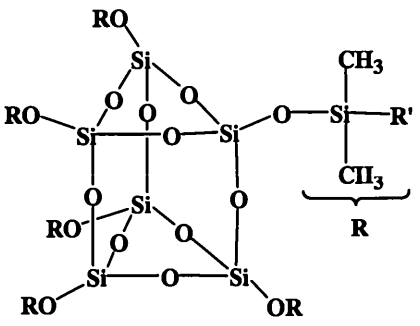
Thus, T_8H_8 was treated with TBAF solution in deuterated chloroform. A great deal of gas was released from the mixture, and then the mixture became very cloudy. After stirring overnight, a solid precipitate was obtained. This was separated from the mixture and the rest of the solution was analysed by NMR. ^1H and ^{13}C NMR shows only peaks for TBAF and no peaks are observed in the ^{29}Si NMR. The white solid was dried under suction. However, owing to its poor solubility in common solvents, the ^{29}Si NMR did not contain any peaks. Since $T_{10}H_{10}$ gives nice crystals and shows a single sharp peak about -86 ppm in deuterated chloroform,[7] this suggested that the rearrangement of T_8H_8 gave silicon resins rather than $T_{10}H_{10}$. The released gas is probably SiF_4 since fluoride ion will react with T_8H_8 to form SiF_4 as a gas.

2.2.3 Summary of the Rearrangement of Octasilsesquioxanes

Octa-5-phenoxypentylsilsesquioxane, 5-phenoxypentylT_8, was rearranged to give a high molecular weight compound using potassium carbonate. On the other hand, the phenoxypentylT_8 cage was degraded to a low molecular weight compound, a monosilyl unit, using sodium trimethylsilanolate. However, other oxygen nucleophiles such as sodium acetate did not show any evidence for the rearrangement of the cage.

TBAF acted as an efficient catalyst for the rearrangement reactions of octasilsesquioxane cages, T_8R_8, with alkyl groups attached to the core. These T_8R_8 cages could be rearranged to higher molecular weight silsesquioxane cages such as $T_{10}R_{10}$ and $T_{12}R_{12}$. The rearrangement of T_8R_8 cages with bulky groups attached to the core did not proceed very well because of the ring strain and structural symmetry. The reaction of octahydrosilsesquioxane, T_8H_8, with TBAF gave a resin rather than cage framework.

2.3 Synthesis and Rearrangement of Spherosilicate Cages



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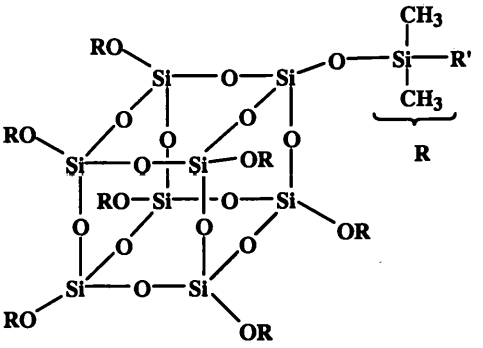


(2.56)

Spherosilicate cages such as compound **2.55** and **2.56**, are silsesquioxane derivatives, where Q represents a silicon atom bonded to four oxygen atoms. T_8R_8 and Q_8R_8 share a similar skeleton based on a cubic cage. The first Q_8R_8 cage appeared in the literature was prepared by Hoebbel and co-worker in 1971.[22] Additional Q_8R_8 compounds have been prepared in recent years. More recently, the encapsulation of atomic hydrogen in a spherosilicate cage, $(SiO_{3/2})_8[OSi(CH_3)_3]_8$, Q_8^M, has been reported, based on irradiation of Q_8^M.

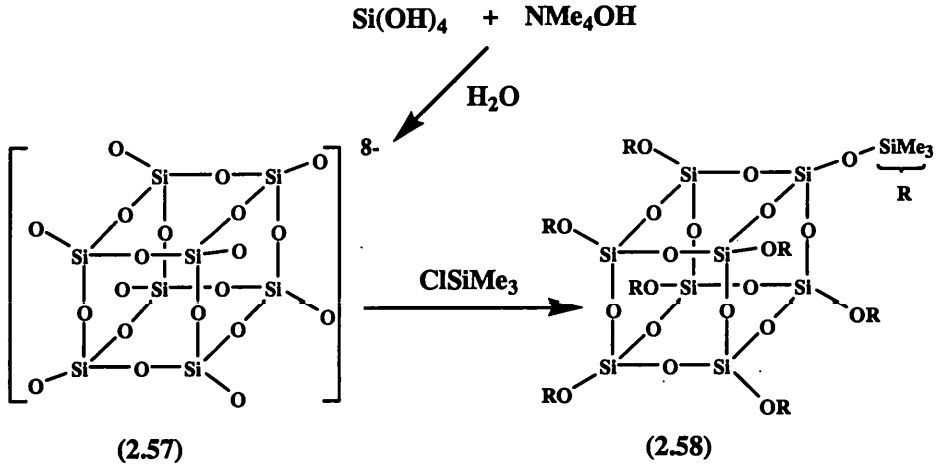
However, the rearrangement reactions of spherosilicates have not been reported in the literature apart from a report by Feher and co-workers, who demonstrated[23] that the Si-O-Si linkage of $(SiO_{3/2})_6[OSi(CH_3)_3]_6$, Q_6^M and Q_8^M could be cleaved by tetraethylammonium hydroxide to give a partial cage.[24] Thus, there is the potential to investigate the rearrangement of these spherosilicate cages further. Spherosilicate cages have an analogous structure to silsesquioxane cages and Marsmann and co-workers have shown[25] that T_8R_8 cages can be successfully rearranged, therefore similar rearrangements should be observed for Q_8R_8 cages. The rearrangement reactions of Q_8^M and Q_6^M were studied in detail because they were easy to prepare and could be obtained in high yield.

2.3.1 Synthesis of Spherosilicate Cages

2.3.1.1 Synthesis of Q_8^M

Q_8^M could be prepared by a two step route, as shown in Scheme 2.36.[26,27]

Tetramethylammonium silicate **2.57**, TMA, was prepared by the condensation of silicic acid and tetramethylammonium hydroxide. A peak at -72.48 ppm in the ^{29}Si NMR spectrum supported the assignment of this compound. The next stage was the formation of Q_8^M **2.58** from TMA. Trimethylchlorosilane was mixed with TMA to give a white solid in 30.6% yield, which could be recrystallised from acetone. ^{29}Si NMR showed peaks at -108.93 ppm arise from the silicon of the cage, and at 12.54 ppm arise from the silicon of the M group attached to the core.[28, 29]



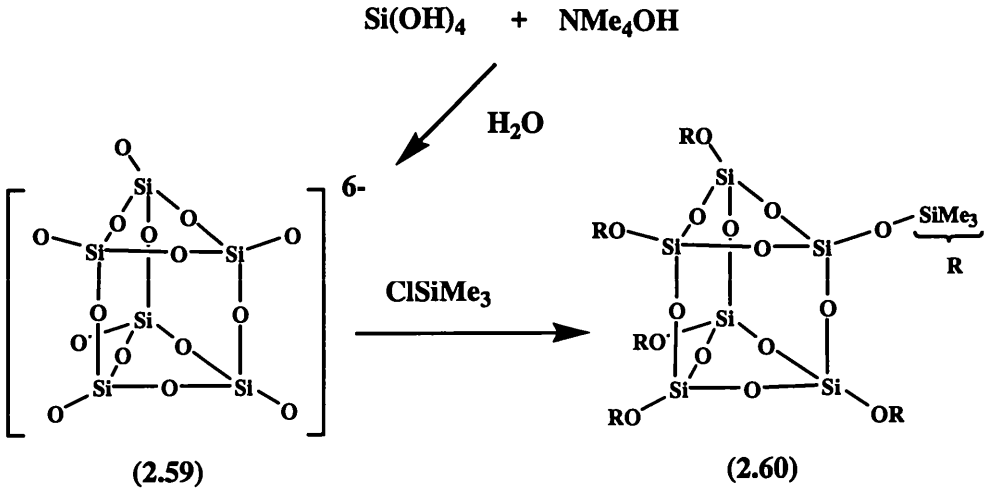
(2.57) (2.58)

Scheme 2.36

2.3.1.2 Synthesis of Q_6^M

Q_6^M was synthesised according to the method of Harrison, which is shown in Scheme 2.37. But the reaction has to be carried out using a polyethylene bottle.[30,31]

The product could be recrystallised from a mixture of acetone and acetonitrile. ^{29}Si NMR shows a peak at -99.32 ppm arising from the silicon of the cage and at 14.29 ppm arising from the silicon of the M group attached to the core. Q_6^M was obtained in 28.6% yield. The crystal structure of Q_6^M has not been reported. Thus a single crystal X-ray crystallographic analysis of this product was carried out.



(2.59) (2.60)

Scheme 2.37

Crystallographic data confirmed the structure of Q_6^M, which is built with 2 Si-O three-membered rings, Si_3O_3, bridged with Si-O-Si linkages, Figure 2.15. For the Si-O three-membered ring, the average Si-O bond length was 1.626 Å and the average Si-O-Si bond angle was 130.19°, which are not very different from those of $Q_6^-[^+NEt_4]$, $Q_6^-[Ni(en)_3^{2+}]$ and other T_6 cages. For the Si-O four-membered ring, the average Si-O bond length was 1.62 Å, which was similar to that of Si-O three-membered ring, but the average Si-O-Si bond angle was 137.52°, again similar to that of $Q_6^-[Ni(en)_3^{2+}]$. The average O-Si-O bond angle was 132.63°, which is much smaller than that of the T_6 cage but similar to that of the $Q_6^-[^+NEt_4]_6$ and $Q_6^-[Ni(en)_3^{2+}]_3$ cages. The OTMS groups on the core are packed as a propeller to the cage.

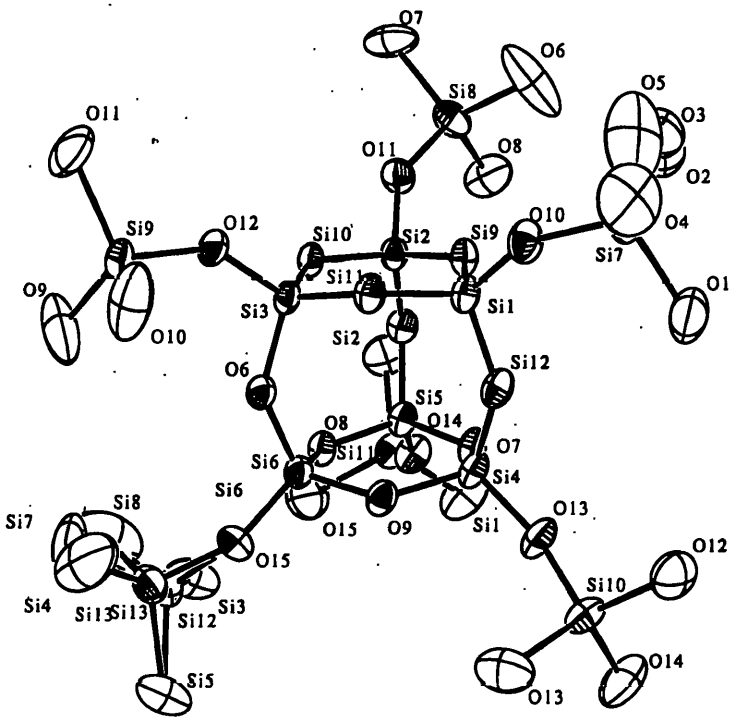


Figure 2.15

2.3.2 Rearrangement of the Q_8^M cage

2.3.2.1 Rearrangement using oxygen nucleophiles

As with the rearrangement of T_8R_8, Q_8^M was rearranged using a series of basic catalysts. These bases were sodium acetate, potassium carbonate and sodium trimethylsilanolate. The reaction mixtures were analysed by ELSD-HPLC and NMR.

a) Rearrangement using sodium acetate

Q_8^M was refluxed with sodium acetate for 24 hours in dry acetone under a nitrogen atmosphere. After removal of the solvent gave a residue and this residue was extracted with dichloromethane. The mixture was filtered and the filtrate was collected. After removal of the solvent, a colourless residue was obtained and analysed by ELSD-HPLC using *iso*-octane and chloroform (10:1) as eluent. Table 2. summarises the retention times of the reaction mixture.

Table 2.10 ELSD-HPLC analysis of rearrangement reaction of Q_8^M using sodium acetate

Peaks	Retention time	Components
Peak1	3.13	Starting material
Peak2	4.16	Product
Peak3	4.53	Product
Peak4	4.96	Product

According to the retention times, peak 1 corresponds to the starting material, Q_8^M, and the other peaks correspond to the reaction products.

Since normal phase HPLC was employed, (the column being a Jones Apex II Silica column), we might expect the components of the reaction mixture to come out in order of their polarity. We expect that the high molecular weight products, Q_{10}^M and Q_{12}^M would be more polar than Q_8^M. So this suggests that the peak of the product in the chromatogram could be the various cages in order of the size. Alternatively, loss of an arm would lead to a silanol, which would also come out later. Further identification was carried out using ^{29}Si NMR. Unfortunately, we were unable to obtain good NMR spectra of these products because the concentration of the reaction products was too low for ^{29}Si NMR.

Marsmann and co-workers has suggested[3] that other non-aqueous solvents can be used, such as dichloromethane, dimethylsulfoxide and acetonitrile. Thus the rearrangement reaction was carried out in dichloromethane. The sodium acetate was filtered off and the dichloromethane removed under vacuum. The residue was analysed by ELSD-HPLC and NMR. However, the results were the same as before. Further modifications to the method and the use of other identification techniques are important goals for the future work.

b) Rearrangement with other basic catalysts

The other basic catalysts used for the Q_8^M rearrangement were potassium carbonate, sodium sulphate, and sodium hydroxide. The reaction mixtures were analysed by ^{29}Si NMR, and ELSD-HPLC, however, the results were inconclusive suggesting that Q_8^M was completely broken down to give resins.

c) Rearrangement with sodium trimethylsilanolate

Q_8^M was refluxed with sodium trimethylsilanolate in dichloromethane for 24 hours. The reaction mixture was analysed by GPC and NMR. Table shows the retention times of the product mixture.

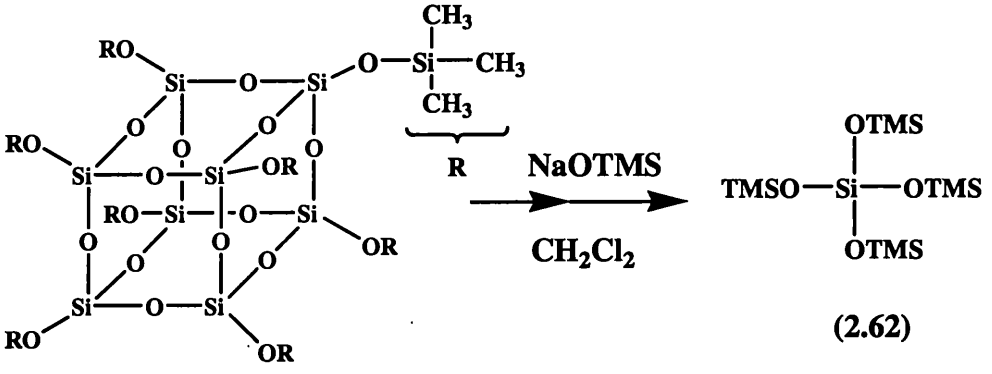
Table 11. Analysis of Q_8^M rearrangement reaction mixture using sodium trimethylsilanolate

Peaks	Retention time	Components
Peak1	4.75	Starting material
Peak2	4.90	Product
Peak3	5.01	Product
Peak4	6.02	Product

Since there are new compounds in the product mixture, a reaction must have occurred. The ^{29}Si NMR of the reaction mixture shows several peaks that could not be assigned, a peak at -92.62 ppm and a group of peaks about 7 ppm together with those of the starting materials, Q_8^M and sodium trimethylsilanolate. In order to remove the peaks arising from sodium trimethylsilanolate, the mixture was treated with trimethylchlorosilane. The ^{29}Si NMR of the resulting solution shows the presence of a new compound with a chemical shift of -104.57 ppm that belongs in the Q-Si region and a group of peaks between 7 and 9 ppm, which belong in the M-Si region. Thus this mixture was spiked with a known M_4Q sample from Dow Corning UK so we could confirmed that the peaks at 8.60 and -104.57 ppm are

from M_4Q **2.61**. The results suggest Q_8^M was degraded to give M_4Q and some other species.

In order to control the degradation of Q_8^M, the reaction was treated with a small amount of sodium trimethylsilanolate to observe the intermediates. The ratio of Q_8^M and sodium trimethylsilanolate was reduced to 1:5. After 6 days reflux, the solvent was removed to give a yellow oily product. The ^{29}Si NMR spectrum, Figure 2.16, shows a group of peaks in the M-Si region between 8 and 12 ppm and a group of peaks in the Q-Si region between -95 and -107 ppm. These results indicate that Q_8^M was degraded gradually to product some partial QM frame works, which eventually gave M_4Q.



(2.62)

Scheme 2.38

However, the NMR spectrum was too complex to identify the intermediates. So far we have not been able to characterise the product. Further identification using electrospray mass spectroscopy was not possible since it did not dissolve in a matrix appropriate for this technique. Conventional mass spectroscopy also proved to be difficult.

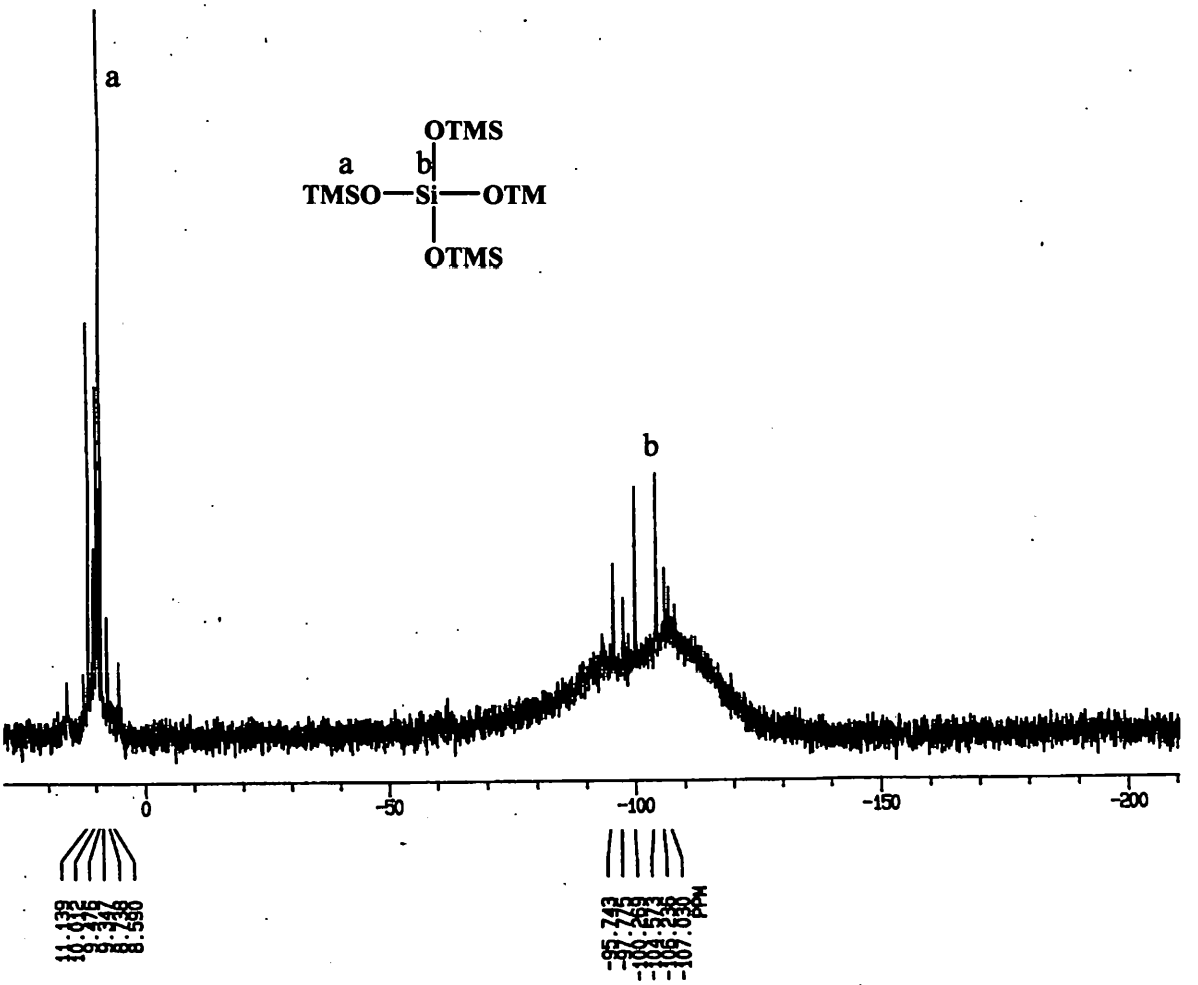


Figure 2.16

2.2.3.2 Rearrangement of Spherosilicates using electrophiles

a) Rearrangement of Q_8^M using triflic acid

The reaction of Q_8^M with triflic acid, TfOH, led to a complete break down of the cage to give, trimethylsilyl triflate, although there was still an evidence of the presence of starting material with a peak at 43.54 ppm in ^{29}Si NMR. It is surprising that no intermediates were observed and the presence of starting material suggests that once one Si-O-Si linkage has been cleaved further breakdown is very rapid. Thus, TfOH was not a suitable catalyst for degradation of Q_8^M.

b) Rearrangement of Q_8^M using a mixture of HBF_4 and BF_3

Q_8^M was treated with a mixture of $HBF_4{\cdot}OMe_2$ and $BF_3{\cdot}OEt_2$, as in the same previous reactions. ^{29}Si NMR showed that the Q_8^M cage had disappeared to form new products

giving rise to two main peaks at 34.87 and 31.42 ppm, two tiny peaks at 20.20 and 15.81 ppm and a triplet at –108.08 ppm. This latter peak indicates that some $MeF_2Si\text{-}O\text{-}SiF_2Me$[14] was formed. However, the peak at 34.87 and 31.42 ppm could not be identified.

2.3.2.3 Rearrangement of Q_8^M and Q_6^M using TBAF

The silicon atoms in spherosilicate cages, Q_6^M and Q_8^M, are connected to four oxygen. This suggests that the silicon atoms in spherosilicate cages should be more electrophilic than that those in silsesquioxanes where each silicon atom is attached to three oxygens. In other words, the reaction of Q_6^M and Q_8^M with fluoride ion should be much faster than with the silsesquioxanes.

a) Treatment of Q_8^M with TBAF

Q_8^M was treated with 0.1 equivalents of TBAF in chloroform at room temperature, in order to control the reaction. After a couple of minutes stirring, the mixture was analysed by ^{29}Si NMR. ^{29}Si NMR showed that no reaction had occurred, giving only two peaks corresponding to the starting material. Thus, the reaction mixture was stirred for a further 24 hours, and analysed by NMR again. ^{29}Si NMR showed there was still no information to show that the reaction had occurred. Therefore, the reaction was repeated using 0.5 equivalents of TBAF solution, after a couple minutes stirring, the reaction mixture was analysed by ^{29}Si NMR. ^{29}Si NMR showed that the Q_8^M cage was degraded to give a species with a group of peaks in the M-Si region between 7 and 12 ppm and a group of peaks in the Q-Si region between -107 and -110 ppm. However, the spectrum was too complex to identify the components. If the reaction was treated with 1 equivalent of TBAF, Q_8^M was broken down completely to give resin. No peak was observed in the ^{29}Si NMR, and some gas was released from the reaction mixture. These results again suggest that Q_8^M cage is much easier to break down than T_6R_6 and T_8R_8 silsesquioxane cages.

b) Treatment of Q_6^M with TBAF

Q_6^M was treated with TBAF, similar to Q_8^M, using 0.5 equivalents of TBAF. After a couple minutes of stirring at room temperature, the reaction mixture was analysed by ^{29}Si NMR. However, ^{29}Si NMR showed the reaction of Q_6^M with TBAF gave resins rather than well-defined QM species.

2.2.3 Summary of the Rearrangement of Spherosilicate cages

A rearrangement reaction of Q_8^M was observed with sodium acetate. Q_8^M rearranged to give low molecular weight compounds. The rearrangement of Q_8^M with potassium carbonate, sodium sulphite and sodium hydroxide gave resins. However, the rearrangement of Q_8^M with sodium trimethylsilanolate led to lower molecular weight compounds such as M_4Q.

TBAF also acts as a catalyst for the rearrangement reaction of spherosilicates, however in this case the cage did not rearrange to give high molecular weight silicate cages, but was degraded to low molecular weight fragments very rapidly.

Therefore, the degradation of spherosilicate cages does occur, but it is not easy to control the reaction.

2.4 Conclusion for Chapter Two

We have synthesised a range of silsesquioxane cages in high yield from the corresponding trialkoxysilanes using TBAF, although the yield of silsesquioxane cages obtained does not make a great deal. Nevertheless, this method provides an efficient one-pot route to the synthesis of silsesquioxane cages in a relatively short time. The mechanism of formation of the silsesquioxane cages is a rather complicated process. We found that the silsesquioxane cage structure is dependent upon the nature of the substituent of the alkyltrialkoxysilane and also upon the solvent, which plays an important role in these reactions. Future work

will focus on isolating and identifying the intermediates and extending the reaction to other functionalities and optimising the reaction conditions.

We studied the rearrangement of octasilsesquioxane cages T_8R_8 with a range of electrophiles, oxygen nucleophiles and TBAF. The rearrangement reaction with TBAF gave the most remarkable results, in which octasilsesquioxane cages were rearranged to give higher molecular weight cages, such as decasilsesquioxane, $T_{10}R_{10}$ and dodecasilsesquioxane, $T_{12}R_{12}$ cages. Again the process is rather complicated involving cleavage of Si-O-Si linkages and subsequent condensation.

We also attempted to apply the TBAF method spherosilicate cages. However, the reaction occurred too rapidly and gave resins due to the eletrophicity of silicon atom in the Q cage. Other catalysts, such as sodium acetate and sodium hydroxide, were also employed for the rearrangement reactions. However, these reactions failed to give well-defined silsesquioxanes. The reaction with sodium trimethylsilanolate also gave complete break-down, which suggests the reaction occurred too quickly. Optimisation of the conditions and/or other catalysts for the cage rearrangement reaction would be interesting for the future work.

2.5 Chapter Two References

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Chapter 3: Synthesis and Rearrangement of Hexasilsesquioxanes

3.0 Introduction

There is not a great deal of work reported in the literature concerning the synthesis and rearrangement of hexasilsesquioxane cages. The hexasilsesquioxane cages, T_6R_6, that have been reported in the literature are summarised in Table 3.1.

Table 3.1 Hexasilsesquioxanes, T_6R_6, cages reported in the literature

$R_6Si_6O_9$, R =	Yield (%)	Ref.
Methyl	_	1, 2
Ethyl	_	3
Cyclohexyl	13	4
	_	5
	10	6
t-Butyl	25	7
Thexyl	41	7
iso-propyl	25	8

The cage structure of the hexasilsesquioxanes, T_6R_6, was first confirmed by X-ray crystallography analysis of hexacyclohexysilsesquioxane, CyT_6, by Molloy and co-workers in 1994.[6] More recently, Unno and co-workers have reported[9,10] the synthesis of T_6R_6, where R = thexyl, *t*-butyl and *iso*-propyl. The trichlorosilane, $RSiCl_3$ (R = thexyl, *t*-butyl and *iso*-propyl), was first hydrolysed to give a silanol species, which was then condensed to give the T_6R_6 cages using DCC in DMSO or DMF.

The first section of this chapter deals with the synthesis of T_6R_6. Here, we report a modified route for the synthesis of CyT_6. Based on this procedure, hexacyclopentylsilsesquioxane, CpT_6, has also been synthesised by the hydrolytic condensation of cyclopentyltrichlorosilane. Other T_6R_6 cages could be synthesised using the DMSO method recently developed in our research group.

The rearrangement reactions of T_6R_6 cages have not appeared in the literature. Feher has demonstrated[11-14] that specific Si-O-Si linkages in hexacyclohexyl silsesquioxane could be cleaved by strong acid, HBF_4/BF_3 and base, tetraethylammonium hydroxide, to give partial cage frameworks. However, there is still a great deal of work that needs to be carried out in this area. The second part of this chapter examines the rearrangement reactions of T_6R_6 cages. Having successfully rearranged a number of T_6R_6 cages, a further series of rearrangement reactions of T_6R_6 were performed in the presence of alkyltriethoxysilanes and other spherosilicate cages and this is discussed in the third part of this chapter.

3.1 Synthesis of Hexasilsesquioxane Cages

The aim of this initial work was to synthesise a series of hexaalkylsilsesquioxane cages. The alkyl groups included cyclohexyl, cyclopentyl, *iso*-butyl, octyl and *p*-methoxyphenylpropyl. Once these well-defined T_6R_6 cages had been successfully synthesised, they would be treated with different catalysts in order to study their rearrangement. The monitoring of these rearrangement reactions and the characterisation of any partial frameworks produced, provided the largest challenge. NMR spectroscopy is the most powerful technique to observe cage degradation or rearrangement and to characterise the products. In addition, High Performance Liquid Chromatography, HPLC, is every useful to monitor the reaction. X-ray Crystallography is obviously the best method of product characterisation when good crystals were available.

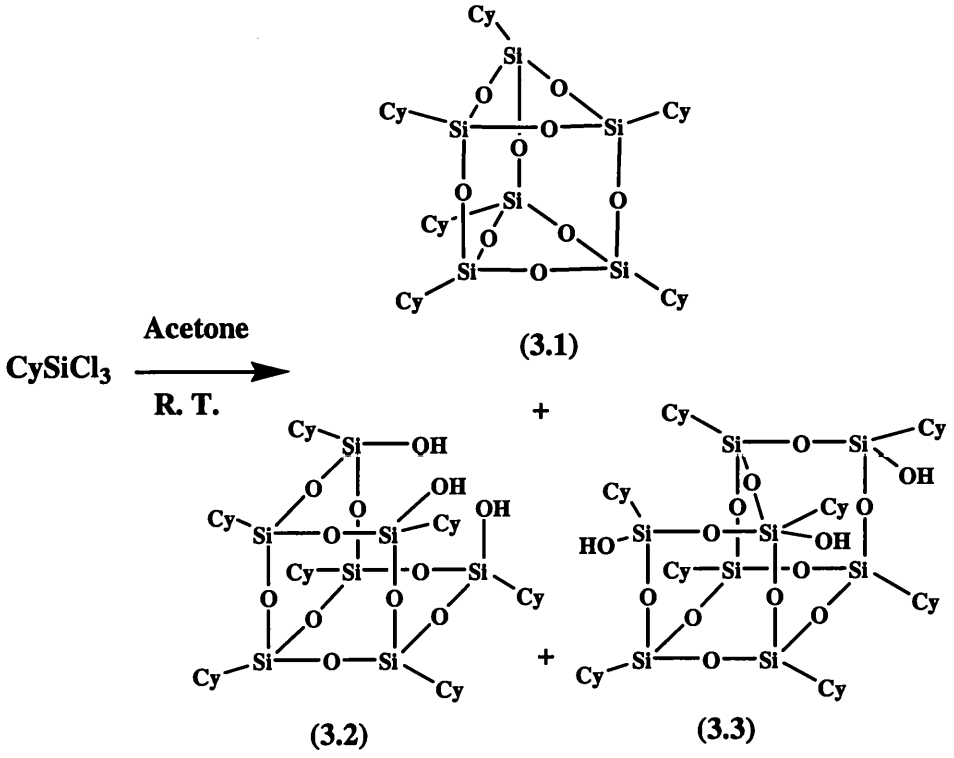
3.1.1 Synthesis of Hexacyclohexylsilsesquioxanes

The reaction used to synthesise hexasilsesquioxanes for our initial work was the hydrolytic condensation of trichlorosilanes, as shown in Scheme 3.1.

$$\underset{\text{Y = OR', Cl}}{nRSiY_3} + 1.5nH_2O \longrightarrow \underset{\text{Oligomeric silsesquioxane}}{R(SiO_{1.5})_n} + 3nHY$$

Scheme 3.1

This synthesis of hexasilsesquioxanes, is potentially very time consuming, taking between 4-36 months. The earliest reported synthetic route to the T_6R_6 was published in 1965 by Brown and co-workers[4] based on the hydrolysis of cyclohexyltrichlorosilane in acetone at room temperature. CyT_6 **3.1** was obtained as part of a mixture with a triol **3.2**, $CyT_7(OH)_3$. Subsequently, Feher and co-workers repeated[5] this reaction, collecting the reaction product after 36 months as shown in Scheme 3.2. CyT_6 was isolated from two other silanol products, $CyT_7(OH)_3$ **3.2** and $CyT_8(OH)_2$ **3.3**, in the reaction mixture using pyridine as solvent, since CyT_6 was insoluble in pyridine.

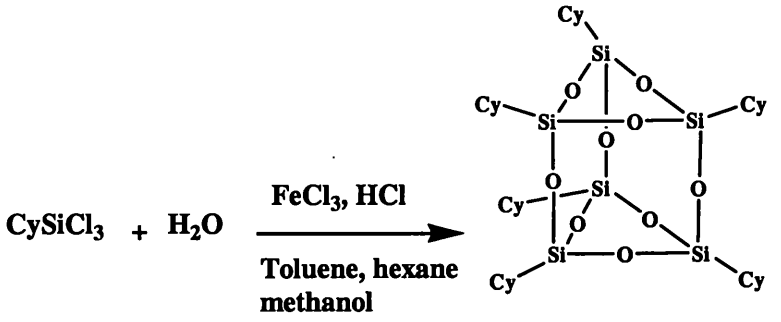


Scheme 3.2

In 1994, Molloy and co-workers modified[6] this synthetic procedure slightly and obtained a high yield of CyT_6 after only leaving the reaction mixture standing at room temperature for 4 months. To improve the efficiency of this reaction and obtain reasonable yields of CyT_6 in a relatively short time, we re-examined both Frye's route[15] to T_8H_8 and Feher's method of CyT_6 synthesis, which both involve a hydrolytic condensation of a trichlorosilane.

a) Hydrolytic Condensation at Room Temperature

The hydrolytic condensation route used by Frye was employed, as shown in Scheme 3.3. However a different solvent system was chosen.

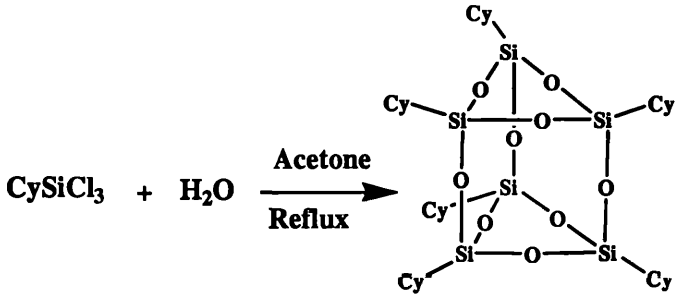


Scheme 3.3

Cyclohexyltrichlorosilane was hydrolysed in concentrated hydrochloric acid with an iron chloride catalyst and a mixed solvent system of hexane, methanol and toluene. The reaction mixture was stirred for 8 hours to complete the condensation. The hexane solution was then separated, and neutralised with sodium carbonate and dried with calcium chloride. A yellow residue was obtained after removal of the solvent. Recrystallisation of the residue in hot hexane gave colourless crystals in 15.9% yield. The crystals gave rise to a single peak at -56.60 ppm in the ^{29}Si NMR. This had a melting temperature of 266°C, in agreement with the literature data for CyT_6 cage. The product was confirmed as the CyT_6 cage using mass spectroscopy, which gave a molecular ion [M^+] at *m/z* 811.42. The advantage of this synthetic procedure is that only a short reaction time is required and the product can be easily to be purified by recrystallisation.

b) Hydrolytic Condensation at High Temperature

The second approach was to modify Feher's route by increasing the reaction temperature, as shown Scheme 3.4.

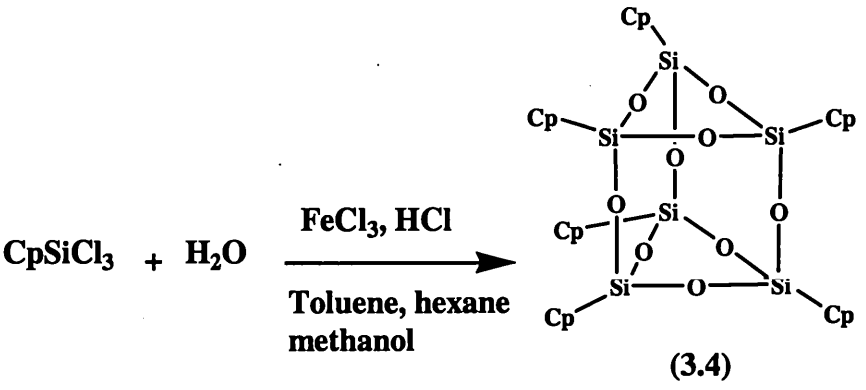


Scheme 3.4

Cyclohexyltrichlorosilane was refluxed with a mixture of water and acetone for 65 hours. A white solid with a yellow oily residue was obtained. After extraction, the product mixture, a white solid, was isolated in 27.8% yield. This white solid had a melting temperature of 266°C, in agreement with the literature data. ^{29}Si NMR confirmed that this white solid was CyT_6, giving a single peak at -56.60 ppm. Spiking this product with that from the modified Frye's route still gave a single peak at -56.60 ppm in the ^{29}Si NMR. The advantages of this method of preparation are a shorter reaction time, and a product that was very easy to purify in relative high yield.

3.1.2 Synthesis of Hexacyclopentylsilsesquioxane

The synthesis of CpT_6, could not be found in the literature. The cyclopentyl and cyclohexyl groups are both alkyl groups with a similar size. Feher had reported[16] that the hydrolytic condensation of cyclopentyltrichlorosilane at room temperature after 7 days gives the partial cage $CpT_7(OH)_3$ rather than the CpT_6 cage. They also indicated that the same product, $CpT_7(OH)_3$, was obtained when the reaction was heated to reflux. Obviously Feher's route would not be suitable for the synthesis of CpT_6 and so Frye's route was used for the hydrolytic condensation of cyclopentyltrichlorosilane, as shown in Scheme 3.5.



Scheme 3.5

Reaction was again carried out in concentrated hydrochloric acid with iron chloride as a catalyst in a mixed solvent of hexane, methanol and toluene. The reaction mixture was stirred for 8 hours to complete the condensation. The hexane solution was then separated and neutralised with sodium carbonate and dried with calcium chloride. A yellow residue was obtained after removal of the solvent. After recrystallisation of the residue from hot hexane, a colourless crystalline material was obtained in 17.8% yield. The ^{29}Si NMR of the crystalline material exhibited a single peak at -54.36 ppm in the T_6R_6 cage region. The melting temperature was 154°C. The mass spectrum showed an [M+] peak at *m/z* 726 and X-ray Crystallography confirmed that the colourless crystal was CpT_6, as shown in Figure 3.1a.

To our best knowledge, this is the first crystalline sample obtained by the method of hydrolytic condensation at room temperature. From the crystallographic data, the compound had crystallised with an orthorhombic crystal system with *Ccca* space group. The CpT_6 cage is built with 2 Si-O three-membered rings, Si_3O_3, bridged with Si-O-Si linkages. The average Si-O bond length and Si-O-Si bond angle for the Si_3O_3 ring (average bond length of Si-O: 1.637 Å and average angle Si-O-Si: 131.27°) are similar to that of Si_3O_3 ring of CyT_6, (average of Si-O: 1.640 Å and average of Si-O-Si: 129.5°)[6] and to that of hexa-*iso*-propylsilsesquioxane, *iso*-propylT_6, (average of Si-O: 1.634 Å and average of Si-O-Si: 130.33°).[10] For the Si_4O_4 ring, the average Si-O bond lengths and Si-O-Si bond

angle for the Si_4O_4 ring (average of Si-O: 1.628 Å and average angle Si-O-Si: 139.08°) are not very different from that of the Si_4O_4 ring in CyT_6, (average of Si-O: 1.625 Å and average of Si-O-Si: 142.3°) and to that of the Si_4O_4 ring of *iso*-propylT_6, (average of Si-O: 1.632 Å and average of Si-O-Si: 139.13°). The average O-Si-O bond angles were 108.73° for CpT_6, which is again similar to that of CyT_6 (average O-Si-O: 108.33 °) and *iso*-propylT_6 (average O-Si-O: 108.12°).

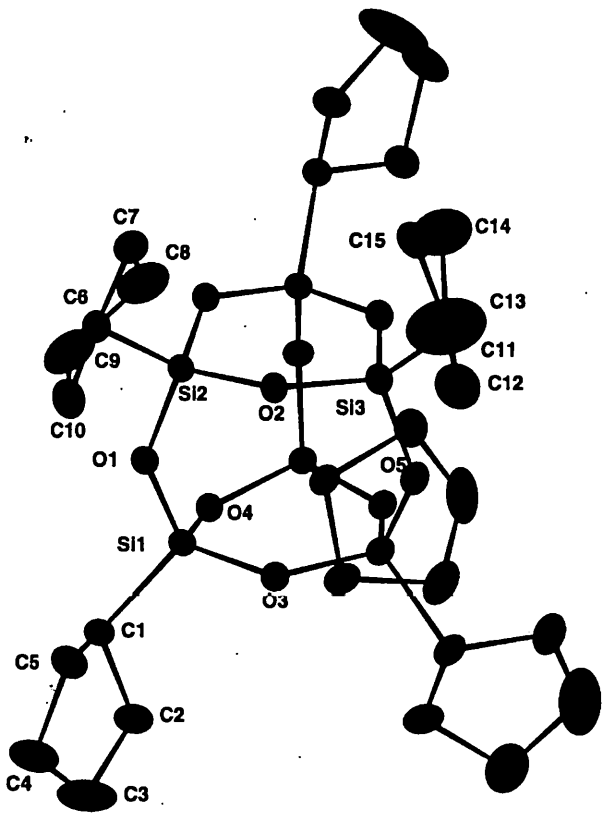


Figure 3.1a

4 cyclopentyl rings are adjacent each other and line on a plane when the other 2 cyclopentyl rings are orthogonal to this plane. This means the cage packs in planes facing each other with the orthogonal cyclopentyl groups interleaved with each other.

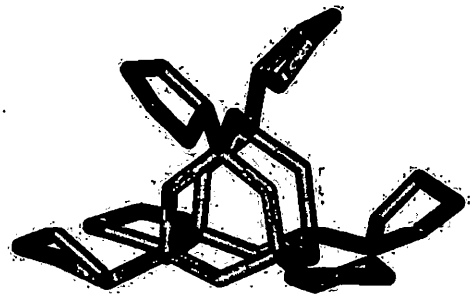
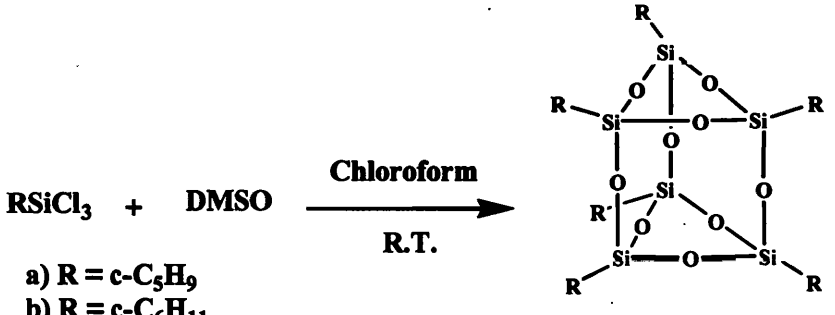


Figure 3.1b

3.1.3 Synthesis of Hexa-*iso*-butylsilsesquioxane

The rate of hydrolytic condensation of trialkylchlorosilanes is dependent upon the length and the branching of the alkyl group at the silicon atom. The rate of condensation was increased when short chain or linear alkyl groups were employed. The *iso*-butyl group is smaller than the cyclohexyl and cyclopentyl groups and so we might expect that the hydrolytic condensation of *iso*-butyltrichlorosilane and its subsequent rearrangement would be faster than that of cyclopentyltrichlorosilane. Thus, the product of the hydrolysis of *iso*-butyltrichlorosilane is most likely to be the octa-*iso*-butylsilsesquioxane, *iso*-butylT_8 or other high molecular weight oligomeric silsesquioxanes rather than the *iso*-butylT_6.

If the hydrolytic condensation is not a very effective method of preparing *iso*-butylT_6, then an alternative routes would be necessary. Our group had investigated[17] the "non-aqueous" condensation of alklytrichlorosilanes using DMSO, as shown in Scheme 3.6.



Scheme 3.6

Reaction of 1 equivalent of trichlorosilanes, $RSiCl_3$, (R = Cy, Cp, octyl, *iso*-butyl, *p*-methoxyphenylpropyl) with 2 equivalents of DMSO afforded T_6R_6 cages together with some DMSO-silicon adducts, in reasonable yields. Whilst isolation of these T_6R_6 from the reaction mixture is often difficult, and the reaction mixture has an unacceptable smell, it is, at present, the most effective method of obtaining the various T_6R_6 cages. Thus, we employed this methodology to obtain T_6R_6 cages. However, to ensure the purity of these cages from the DMSO method, the purification procedure was modified. The reaction was carried out using *iso*-butyltrichlorosilane and DMSO in chloroform for 24 hours to give the *iso*-butylT_6 in 19.2% yield. The product was purified by flash chromatography, firstly using an alumina column with a mixed solvent of chloroform and hexane (1:1), and secondly by recrystallising very slowly from a mixed solvent of hexane and chloroform (4:1) to give a pure waxy product. ^{29}Si NMR showed a single sharp peak at -55.83 ppm and mass spectroscopy revealed an M^+ peak at *m/z* 654, confirming the product is *iso*-butylT_6 **3.5c**.

3.1.4 Synthesis of Hexaoctylsilsesquioxane

Since the octyl group has a linear 8-carbon chain, substitution at the silicon of the corresponding chlorosilane should occur more readily than with the cyclopentyl or cyclohexyltrichlorosilanes. Thus, the hydrolytic method of condensation would lead to larger cages. The synthesis of OctylT_6 **3.5d**, again focussed on the "non-aqueous" condensation method. The octyltrichlorosilane was added to DMSO in chloroform and the reaction monitored by ^{29}Si NMR spectroscopy. After 24 hours, ^{29}Si NMR showed the disappearance of octyltrichlorosilane and the appearance of a new single peak at -54.18 ppm. The reaction was stopped and a yellow oily product was obtained after removal of the solvent. This product was purified by flash column chromatography using alumina with a mixture of hexane and chloroform (1:1) as the eluent, followed by recrystallisation from a

mixed solvent of chloroform and acetone (1:2) to give OctylT_6 **3.5d** as a wax in 4.2% yield.

3.1.5 Synthesis of Hexa-*p*-methoxyphenylpropylsilsesquioxane

For the similar reasons, the "non-aqueous" condensation method was employed for the synthesis of *p*-methoxyphenylpropylT_6 **3.5e**. The *p*-methoxyphenylpropyltrichlorosilane was added to DMSO in chloroform and the reaction monitored by ^{29}Si NMR spectroscopy, which showed the disappearance of *p*-methoxyphenylpropyltrichlorosilane and the appearance of a single peak at -54.42 ppm. After about 24 hours stirring, the reaction was stopped and gave a yellow oily white product after removal of the solvent. The product was purified by extraction with acetone and recrystallisation from chloroform to give *p*-methoxyphenylpropylT_6 **3.5e** as a colourless crystal in 12.5% yield. Single crystal X-ray crystallographic analysis confirmed the structure. The compound had crystallised with a monoclinic crystal system and a *C2/c* space group. As before the *p*-methoxyphenylpropylT_6 cage was built with 2 Si-O three-membered rings, Si_3O_3, bridged with Si-O-Si linkages, Figure 3.2. For the Si-O three-membered ring, the average Si-O bond length (1.635 Å) and the average Si-O-Si bond angles (130.82°) are very similar to that of other T_6R_6 cages. For the Si-O four-membered ring, the average Si-O bond length (1.626 Å) is also very similar to that of other T_6R_6 cages, but the average Si-O-Si bond angles (140.05°) were slightly bigger. By contrast, the O-Si-O angles (107.36°) were slightly smaller than those of other T_6R_6 cages. It is remarkable that the *p*-methoxyphenylpropyl groups on the core pack very tightly with in a linear fashion. When one of the phenyl rings lines in a plane, the other 2 phenyl rings on the same Si_3O_3 ring are parallel each other and are orthogonal to this plane. This means the cages pack facing each other with the phenyl rings vertical to each other.

The liquid crystal properties of compound based on T_8R_8 cage with mesogen arm is thought to arise from them adopting a similar elongated form, thus this crystal structure supports this hypothesis.[18] The corresponding *p*-methoxyphenylpropylT_8 cage has a similar elongated form as does the octylT_8.[19]

Table 3.2 summarises the Si-O bond lengths and Si-O-Si and O-Si-O bond angles of the different T_6R_6 cages.

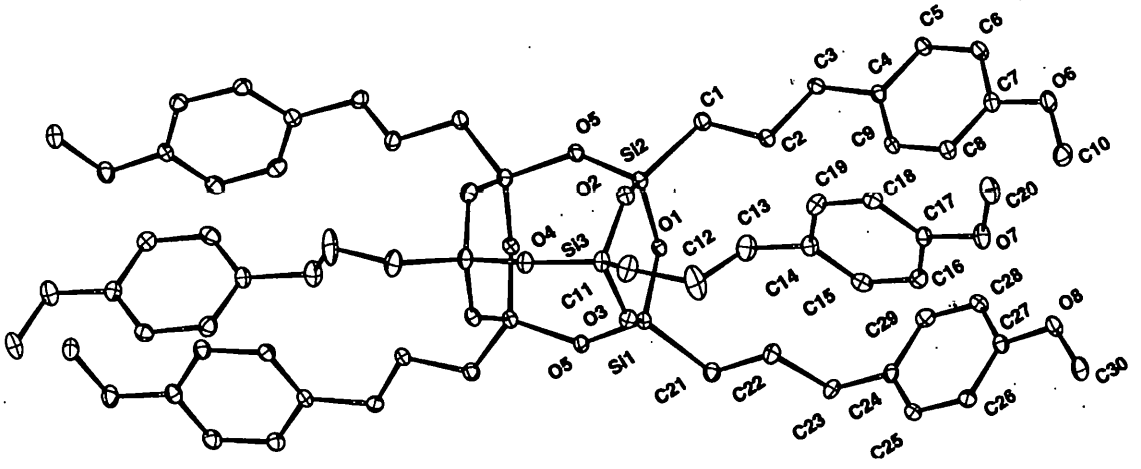


Figure 3.2

Table 3.2 Comparison of Bond length and angles of T_6R_6 cages

T_6R_6, R =	Si_3O_3 ring		S_4O_4 ring		O-Si-O (°)	Ref.
	Si-O (Å)	Si-O-Si (°)	Si-O (Å)	Si-O-Si (°)		
Cyclopentyl	1.637	131.27	16.279	139.08	108.73	This work
p-methoxyphenylpropyl	1.635	130.82	1.625	140.05	107.36	This work
Cyclohexyl	1.640	129.50	1.625	142.33	108.33	6
Iso-propyl	1.635	130.33	1.632	139.13	108.12	8

In summary, a range of T_6R_6 cages, R = cyclohexyl, cyclopentyl, *iso*-butyl, octyl and *p*-methoxyphenylpropyl, have been synthesised. However, different synthetic approaches had to be used for different cages because of the nature of the R groups on the core. Table 3.3 summarises the yields of the T_6R_6 from the corresponding trichlorosilanes.

Table 3.3 The yields of T_6R_6 using different methods

$R_6Si_6O_9$, R=	Method*	Time (Hour)	Yield (%)
Cy	A	8	15.9
	B	65	27.8
Cyclopentyl	A	8	17.8
Iso-butyl	C	24	19.2
Octyl	C	24	4.2
p-methoxyphenylpropyl	C	24	12.5

*Method: A - hydrolytic condensation at room temperature; B - Hydrolytic condensation at high temperature; C - "Non-aqueous" hydrolysis of corresponding trichlorosilane.

3.2 Rearrangement of Hexasilsesquioxanes

The rearrangement of hexasilsesquioxanes, T_6R_6, was carried out using a range of catalysts. ^{29}Si NMR "stack experiments" and HPLC were used to monitor the reactions with TBAF. CyT_6 was chosen first for the ^{29}Si NMR "stack experiments" because ^{29}Si NMR information is available on many cyclohexyl cages and partial cages. The rearrangement of other hexasilsesquioxanes, such as cyclopentyl, *iso*-butyl, octyl, and *p*-methoxyphenylpropyl, were also examined using "stack experiments". ^{29}Si NMR spectra were collected every two hours for a period of 16 hours. Whilst the NMR spectra showed the disappearance of the starting materials and the formation of the octasilsesquioxanes, T_8R_8, they did not provide any more information on the intermediates. This could be due to a number of reasons:

1) The ^{29}Si abundance is only about 4% thus many scans are needed to obtain reasonable spectra in which minority species can be identified. This was not possible during a "stack experiments".

2) Many of the alkyl groups mentioned above are less bulky than the cyclohexyl group, thus, the formation of closed cage species from partial cage intermediates would be much faster for these groups than with cyclohexylhexasilsesquioxane.

3) The intermediate could be a loose resin or ladder, which would give rise to many peaks, which would be lost in the baseline.

Thus, ^{29}Si NMR spectroscopy could not be used to obtain information on intermediates that had a relatively short lifetime.

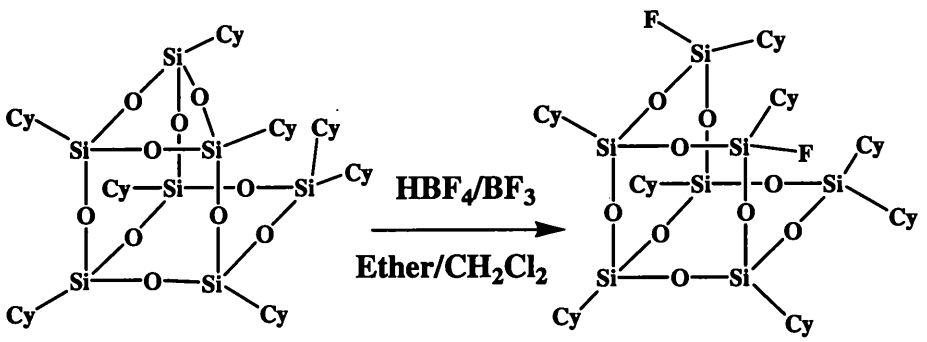
An alternative approach to identifying these intermediates is to stop the rearrangement reaction after a certain time and to analyse the reaction mixture.

3.2.1 Rearrangement of Hexacyclohexylsilsesquioxane

3.2.1.1 Using electrophiles

a) Using HBF_4/BF_3

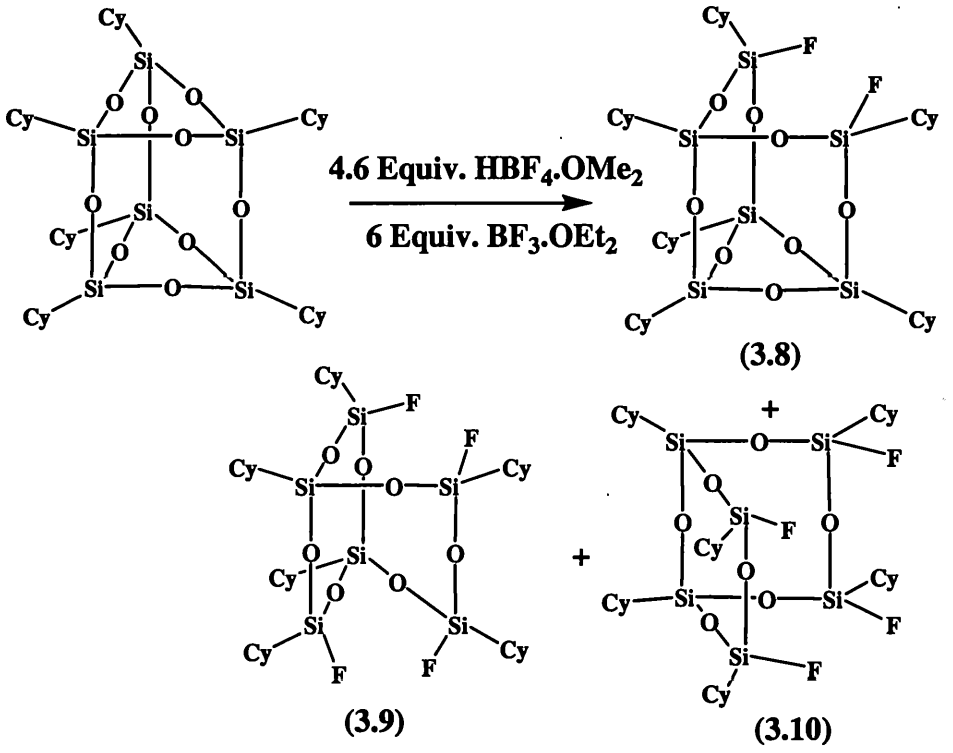
Feher and co-workers first reported[13] the degradation of CyT_7, **3.6**, using excess of HBF_3/BF_4. They demonstrated that the Si-O-Si linkage of the Si-O three-membered ring, Si_3O_3, was cleaved faster than that of the Si-O four-membered ring, as shown in Scheme 3.7



(3.6) (3.7)

Scheme 3.7

Thus, with the CyT_6, one of the Si-O-Si linkages within the Si_3O_3 ring was cleaved first to give a difluoride adduct. This difluoride species **3.8** was a precursor of the tetrafluoride product **3.9** and **3.10** for which two Si-O-Si linkages, both within Si_3O_3 rings, were cleaved, as shown in Scheme 3.8.



Scheme 3.8

We repeated this reaction in order to build up a library of spectroscopic data on the cleavage products of CyT_6. The reaction was carried out at room temperature using a mixture of 4.6 equivalents $HBF_4.OMe_2$ and 7 equivalents $BF_3.OEt_2$. ^{29}Si NMR showed that there are only two products observed along with some starting materials. When a reduced amount of $HBF_4.OMe_2$ (1.5 equivalents.) and $BF_3.OEt_2$ (2.3 equivalents) was used another unknown product was observed alongside these two products and some starting material. We repeated this reaction at a higher temperature, using 4.6 equivalents of $HBF_4.OMe_2$ and 6 equivalents of $BF_3.OEt_2$. The ^{29}Si NMR spectrum suggested that the Si-O-Si linkages of CyT_6 were cleaved to give three different cage structures. Two products **3.9** and **3.10** were identical to those obtained by Feher and co-workers but the third product had not been reported. We have tried to isolate and purify this unknown product, but as yet we have not been successful.

The reaction was repeated and monitored regularly using ^{29}Si NMR in order to observe the order in which the species are formed. CyT_6 was dissolved in deuterated chloroform with 6

equivalents of $HBF_4.OMe_2$ and 6 equivalents of $BF_3.OEt_2$ in a 5 mm NMR tube. The reaction mixture was stirred for a few minutes and then analysed by ^{29}Si NMR. The spectra were collected every hour for a period of 15 hours, as shown in Figure 3.3.

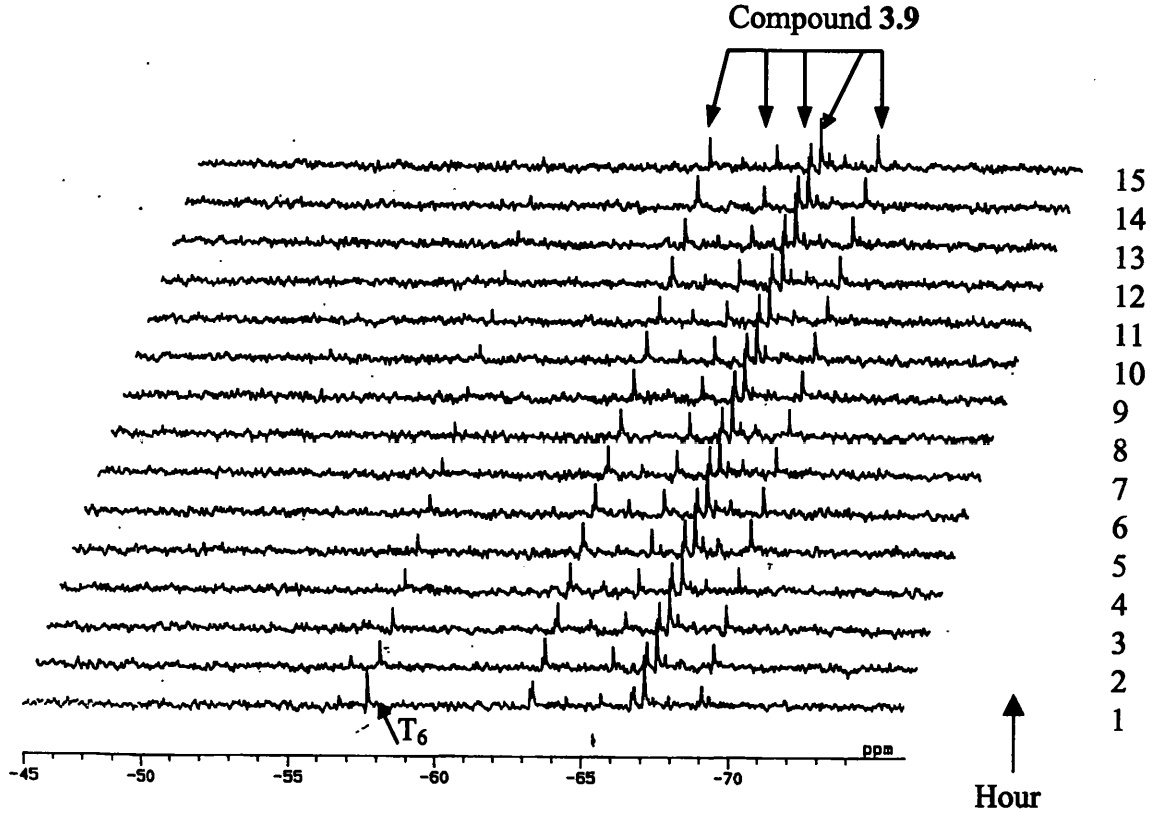
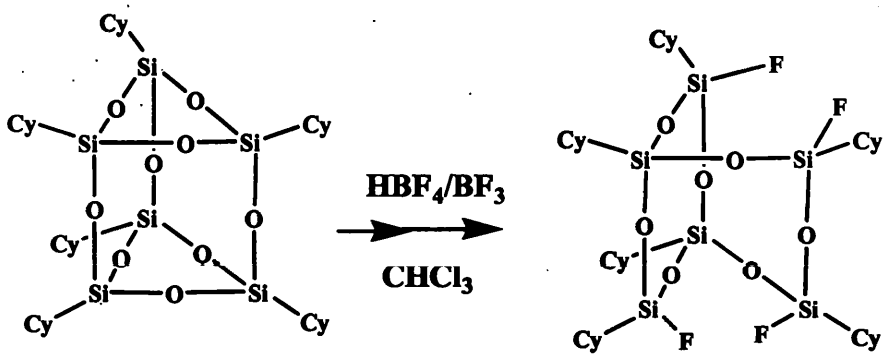


Figure 3.3

^{29}Si NMR showed reaction occurs very rapidly and the CyT_6 can be seen to decrease quickly with time. After an hour, a new product appeared. After 15 hours, the CyT_6 was almost completely consumed. Although it was not possible to identify all the peaks in the spectra, it was obvious that one of the products, the tetrafluoride **3.9** dominated the spectrum giving arise to the peaks in the ratio 2:2:2, Figure 3.4. It was also clear that these peaks increased at the expense of CyT_6 and other intermediates, Scheme 3.9.



Scheme 3.9

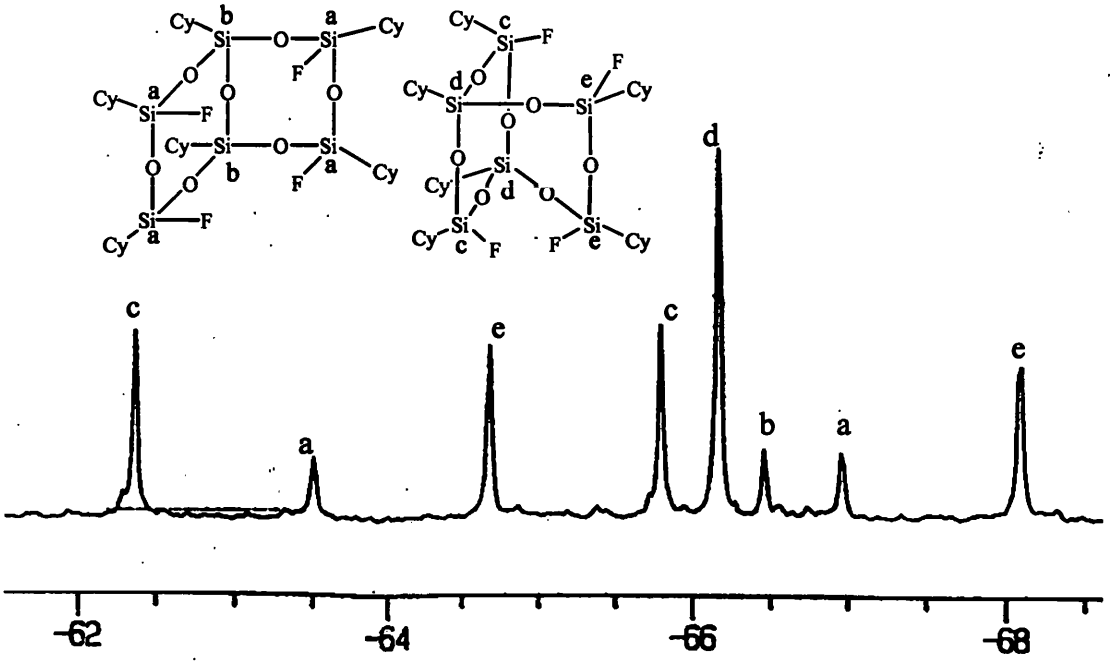
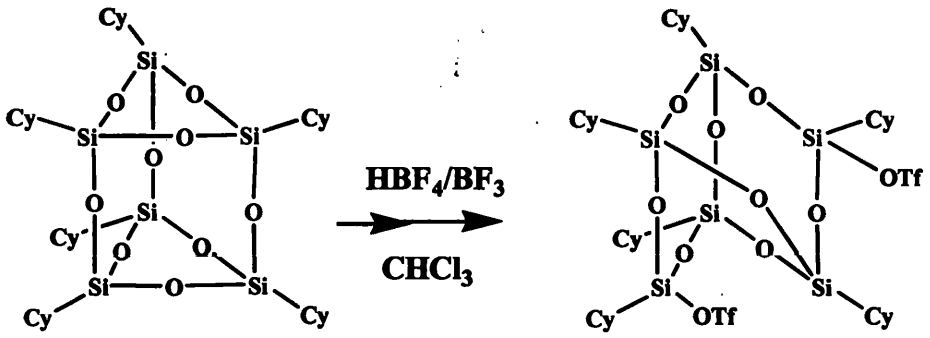


Figure 3.4

b) Using Triflic Acid

The reaction of CyT_6 with triflic acid, TfOH, that published by Feher and co-workers,[12] was repeated using different solvents. We obtained the similar outcomes as Feher using deuterated chloroform as the solvent, as shown in Figure 3.5. Ditriflate **3.11** was obtained along with other unknown products.



(3.11)

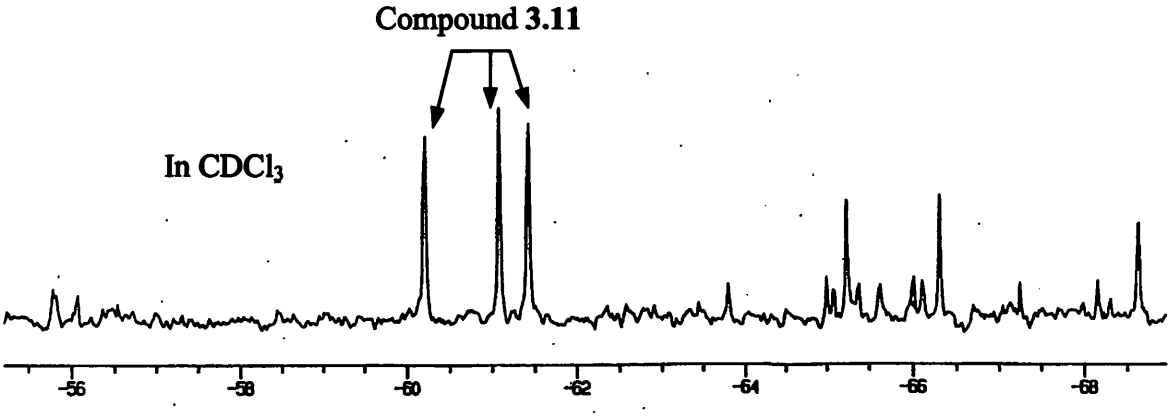


Figure 3.5

However, if the reaction performed in deuterated benzene, the reaction gave different outcomes, as shown in Figure 3.6. A group of peaks appear between -55 and -68 ppm, which could not be identified, in spite of the simple pattern of the peaks. We believed that the CyT_6 cage had been degraded to form partial cage species.

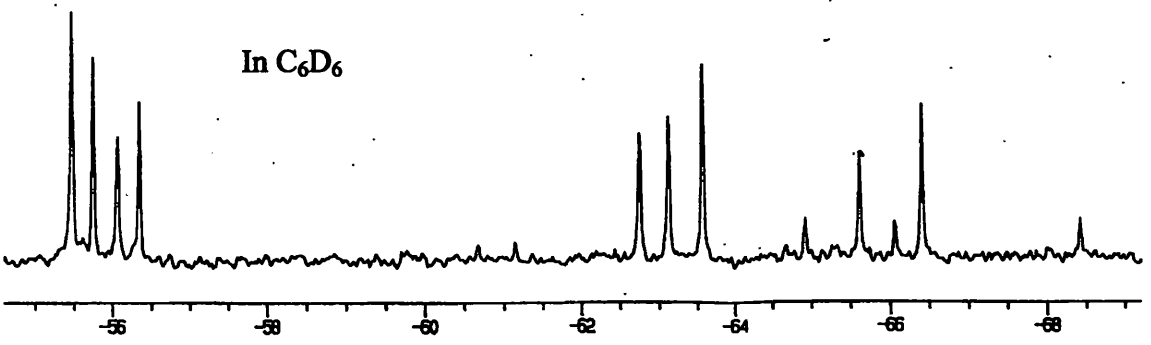


Figure 3.6

3.2.1.2 Using oxygen nucleophiles

CyT_6 was used as a model for the reaction with oxygen nucleophiles since the preparation of CyT_6 is very easy and purification is simple.

a) Using sodium acetate

CyT_6 was refluxed with sodium acetate in acetone for a day. The reaction mixture was analysed by ^{29}Si NMR, which showed the presence of unreacted CyT_6 starting materials. Only a small amount of product was observed. From the chemical shifts, it seemed that the CyT_6 had rearranged to give the higher molecular weight cage CyT_8. However, the amount of CyT_8 was relatively small compared to the amount of resin formed. These results suggested that sodium acetate was not an appropriate catalyst for the rearrangement of CyT_6.

b) Using potassium carbonate

Potassium carbonate was another catalyst used for the rearrangement of T_8R_8.[20] CyT_6 and potassium carbonate were refluxed in acetone for a day and after removal of the solvent, an oily residue was obtained. The ^{29}Si NMR spectrum of the residue exhibited no obvious peaks. However, this residue formed needle-like crystals on standing at room temperature. The ^{29}Si NMR suggested these crystals were a very complex mixture, with numerous peaks between -56 and -72 ppm. Although MALDI-TOF mass spectroscopy showed two main species at *m/z* 972 and 1063 ($M+Ag^+$), this was still not enough information to fully characterise the products.

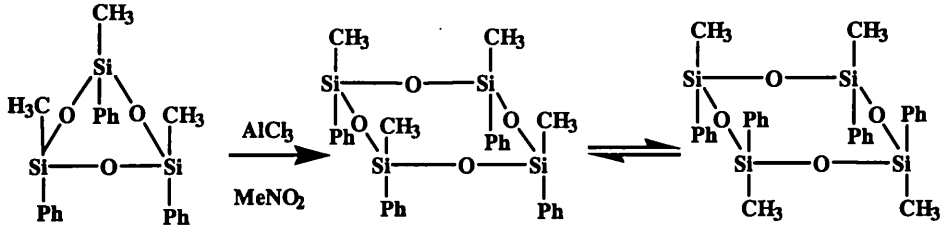
c) Using sodium trimethylsilanoate

In previous chapter, we described the degradation of T_8R_8 with sodium trimethylsilanolate to give a monomer, T unit, and Q_8^M degradation to a M_4Q species. Thus, CyT_6 was treated with sodium trimethylsilanolate in order to observe whether it would give similar products. CyT_6 and sodium trimethylsilanolate were refluxed in dichloromethane for a day. The

reaction mixture was washed with saturated sodium bicarbonate solution. After removal of the solvent from the organic layer, an oily residue was obtained. ^{29}Si NMR showed a group of peaks between 6 and 8 ppm, which indicated the presence of the $OSiMe_3$ group. Another group of peaks appeared between -67 and -72 ppm, in the T-Si cage region. Since the CyT_6 had disappeared, it must have rearranged to higher molecular weight cages. However, the degradation product could not be identified because of the complex ^{29}Si NMR.

3.2.2.1 Using Lewis acids

Lewis acids had previously been used to rearrange D_3 to two D_4 isomers,[21] *cis* and *trans*, as shown in Scheme 3.10.



Scheme 3.10

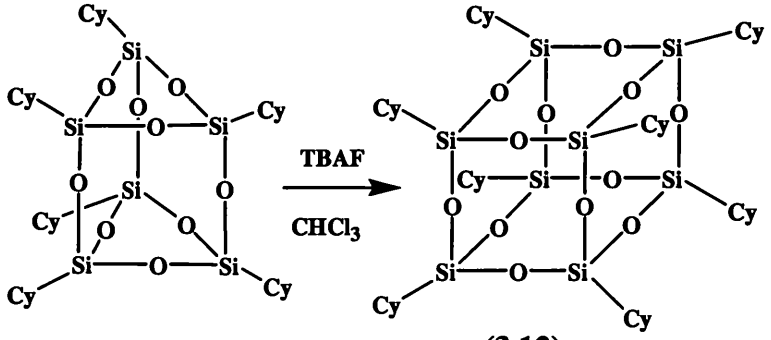
Thus, Lewis acids may have a similar effect on T_6R_6 cages. CyT_6 was refluxed for 24 hours with aluminium chloride in nitromethane. After removal of the solvent the reaction mixture gave a white solid . ^{29}Si NMR showed only one peak at -56.60 ppm, which is identical to the starting material CyT_6. Another Lewis acid, iron chloride was also tried but still gave unreacted CyT_6.

Such results demonstrate that ring strain plays an important role in this kind of reaction. The ring strain in D_3 is sufficient to cause rearrangement to larger rings such as D_4, D_5 and D_6. However, the ring strain of the 3-membered Si-O rings in the T_6R_6 cage seem to be less important than in the corresponding monocyclic compound because of the cage structure.

3.2.2.3 Using TBAF - initial study

In chapter 2, it was demonstrated that TBAF was an excellent catalyst for the rearrangement of octasilsesquioxanes to give higher molecular weight cages. Thus, an obvious progression was to react TBAF with the T_6R_6 cages.

CyT_6 was dissolved in deuterated chloroform, and the mixture treated with 2 equivalents of TBAF. After stirring overnight at room temperature, the reaction mixture was analysed by ^{29}Si NMR. The ^{29}Si NMR spectra indicated that the CyT_6 had rearranged to the higher molecular weight product **3.12,** CyT_8 at 34.7%, which gives arising to a single peak in the T_8-Si region, at -68.69 ppm, Scheme 3.11.



(3.12)

Scheme 3.11

In order to investigate the details of the rearrangement from CyT_6 to CyT_8. A "stack experiments" in which the reaction was monitored by ^{29}Si NMR was carried out. NMR spectra were collected each hour for a period of 50 hours, as shown in Figure 3.7. CyT_6 was seen to disappear within an hour and a group of peaks appeared between -68 and -71 ppm, together with a smaller group of peaks at about -59 ppm. The CyT_8 cage appeared after 2 hours and increased at the expense of the other intermediates.

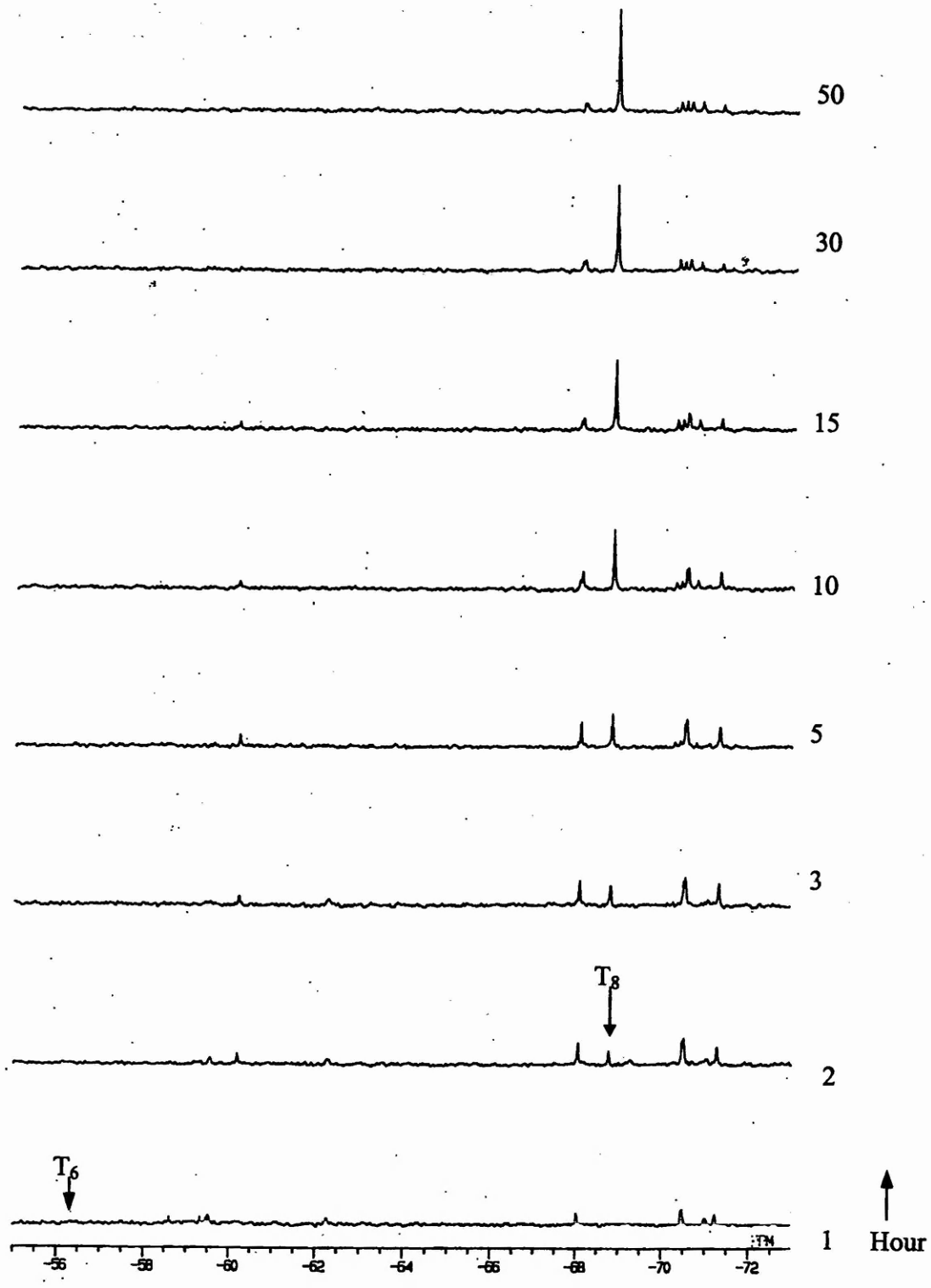


Figure 3.7

a) Rearrangement of Hexacyclohexylsilsesequioxane - in more detail

CyT_6 was used as a model for the reaction of T_6R_6 with TBAF in order to identify the intermediates involved in the rearrangement from T_6R_6 to T_8R_8. The main reason for

choosing CyT_6 was that more spectral information was available in the literature on the corresponding partial or closed cage structures.

i) Monitoring the rearrangement reaction using ^{29}Si NMR

The previous "stack experiments" indicated that the reaction occurred very quickly with 2 equivalents of TBAF. In order to slow down the reaction and obtain more information about the intermediates, another "stack experiments" was carried out, to study the rearrangement process in detail. Thus, T_6R_6 was mixed with 0.5 equivalents of TBAF in deuterated chloroform in a 5 mm NMR tube. The mixture was stirred for a few minutes and the ^{29}Si NMR spectra were collected every 2 hours over a period of 16 hours. The spectra in Figure 3.8 suggest that the intermediates are formed within 2 hours. After 4 hour, CyT_8 and a major intermediate were observed. This indicates that such intermediates could be identified more easily by controlling the reaction time.

In an attempt to isolate the intermediates from the reaction mixture the reaction was repeated on a larger scale and stopped after 4 hours, by removal of the TBAF with water. The organic layer was separated and a white solid obtained after removal of the solvent. Two components were obtained using a silica column with a mixed solvent of chloroform and hexane (1:3) as the eluent. ^{29}Si NMR spectra suggested that the first fraction was CyT_8, giving a peak at -68.69 ppm and the second fraction was CyT_9OH **3.13**, which has 5 peaks at -59.27, -67.81, -70.04, -70.32, and -70.60 ppm in a ratio of 1:2:2:2:2. The identification of this CyT_9OH **3.13** was also confirmed by mass spectral data and X-ray crystallographic analysis.

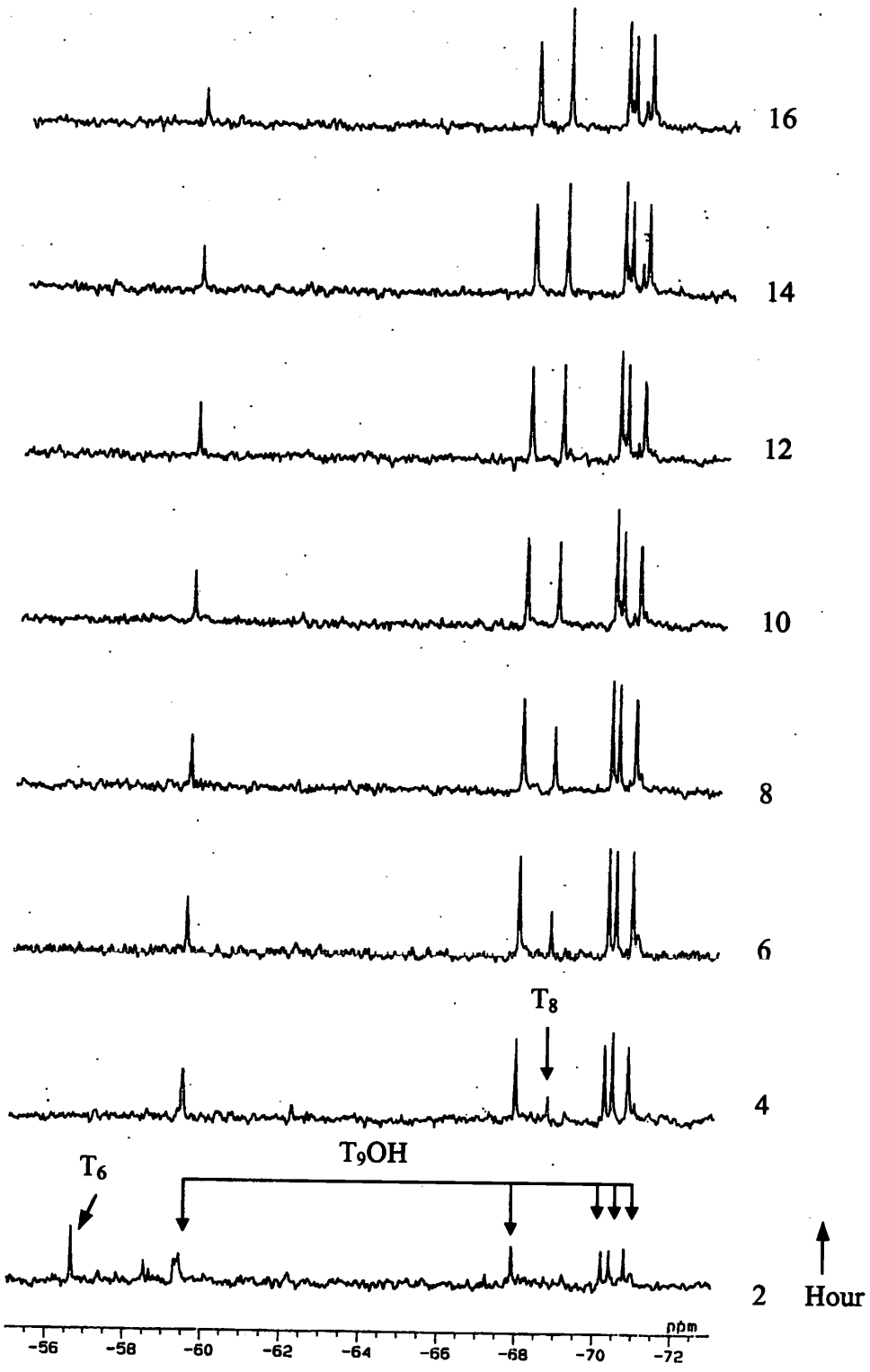


Figure 3.8

This is the first example of a T_9R_9OH silsesquioxane cage obtained from the rearrangement reaction of T_6R_6, as shown in Figure 3.9.

From the crystallographic data, CyT_9OH is built from 2 Si-O five-membered rings and 4 Si-O four-membered rings. The average Si-O bond length in the Si-O five-membered ring

and the Si-O four-membered ring are very similar to each other (1.620 Å for the Si-O five-membered ring and 1.61 Å for the Si-O four-membered ring). On the other hand, the Si-O-Si bond angles were 152.27 for the Si-O five-membered ring and 147.64° for the Si-O four-membered ring. The average O-Si-O bond angles were 109.08°, which is not very different to those in the T_8R_8 silsesquioxane cages (*ca* 108.91°), and T_6 cage (108.12°). The cyclohexyl rings are packed as a propeller to the cage.

In a further experiment, the CyT_9OH was silylated with excess TMSCl, the ^{29}Si NMR showed that the Si-OH peak at -59.27 shifted to -68.99 ppm corresponding to a Si-O-TMS group of product **3.14**, CyT_9OTMS. This structure was also confirmed X-ray crystallography, Figure 3.10.

The O-Si bond length (1.615 Å for the Si-O five-membered ring and 1.608 Å for the Si-O four-membered ring) are similar to that of CyT_9OH. On the other hand, the Si-O-Si bond angles (157.23° for the Si-O five-membered ring and 148.11° for the Si-O four-membered ring) are slightly bigger than before the silylation. The average O-Si-O bond angle is 109.15°, as the same as before the silylation. Again, the cyclohexyl groups are pack as a propeller to the cage. Table 3.4 shows a comparison of the bond length and angles of CyT_9OH and CyT_9OTMS.

Table 3.4 Comparison of bond lengths and angles of CyT_9OH and CyT_9OTMS

	Si-O five-membered ring		Si-O four-membered ring		O-Si-O (°)
	Si-O (Å)	Si-O-Si (°)	Si-O (Å)	Si-O-Si (°)	
T_9OH	1.612	152.27	1.620	147.64	109.08
T_9OTMS	1.608	157.23	1.615	148.11	109.15

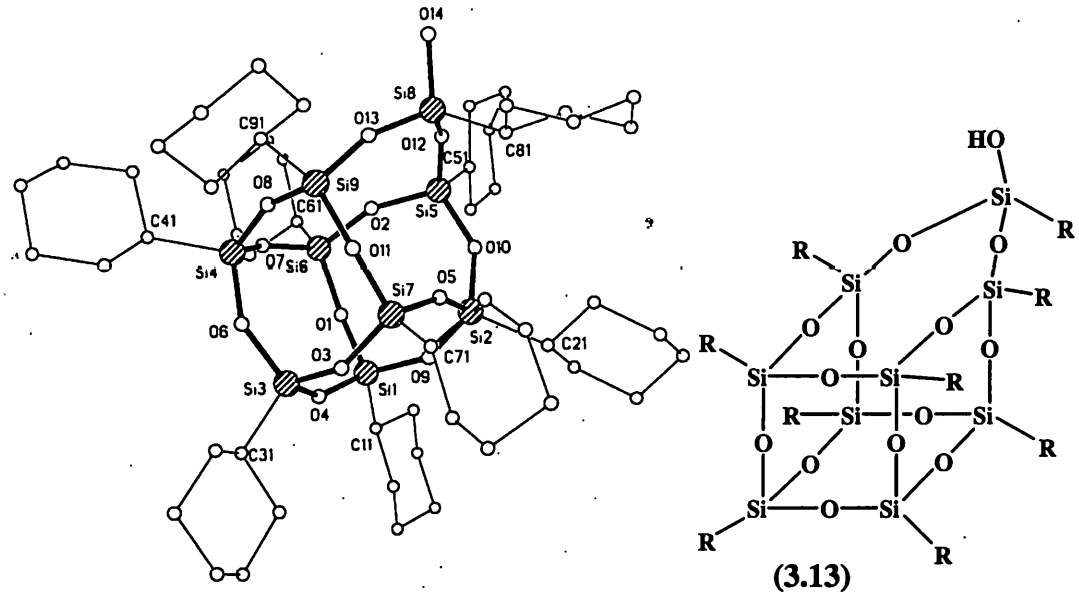


Figure 3.9

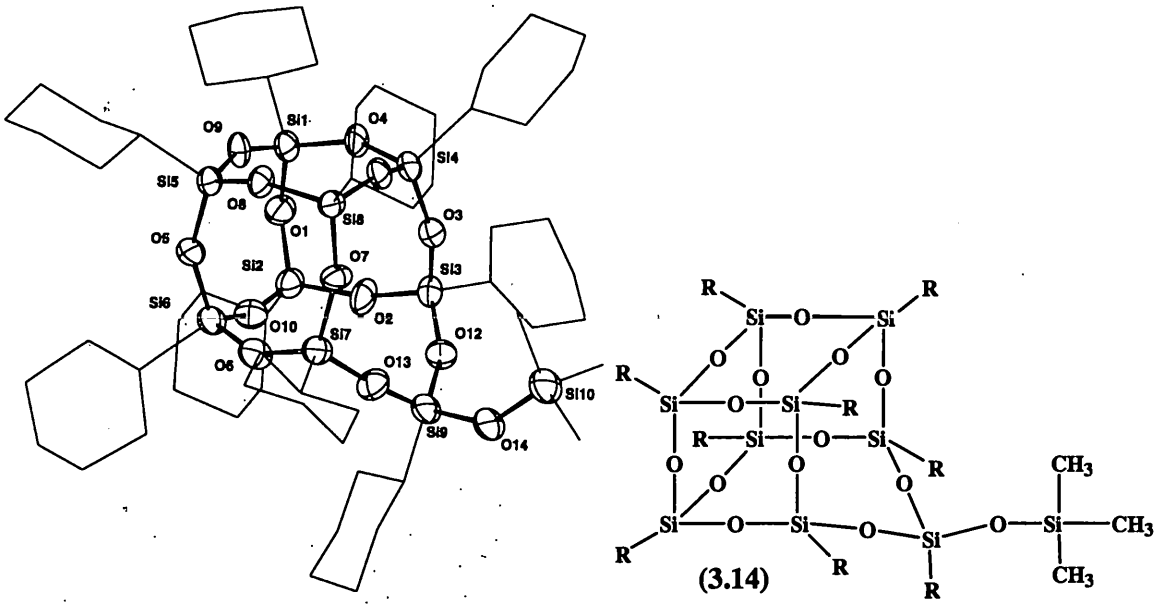


Figure 3.10

ii) Monitoring the rearrangement reaction using HPLC

HPLC was used to monitor CyT_6 rearrangement reaction and to isolate the other intermediates using *iso*-octane and chloroform as eluent with a silica column (5μ) and an ELSD detector. Unfortunately, no new compounds were obtained which give arising to any signals in the ^{29}Si NMR. It is possible that the intermediates may have contained too many

OH groups and thus adhered to the column. An indication of the extent of the missing material may be obtained from the mass balance calculation based on the quantity of CyT_6, CyT_8 and CyT_9OH measured using calibration curves. Figure 3.11 shows that, under these conditions, CyT_6 decreased rapidly and disappeared in a couple hours. At the same time an intermediate built up at the expense of the CyT_6. After 1 hour, CyT_9OH is formed and the amount of the unknown intermediate falls off. After 4 hours, CyT_8 is produced at the expense of CyT_9OH and the unknown intermediate.

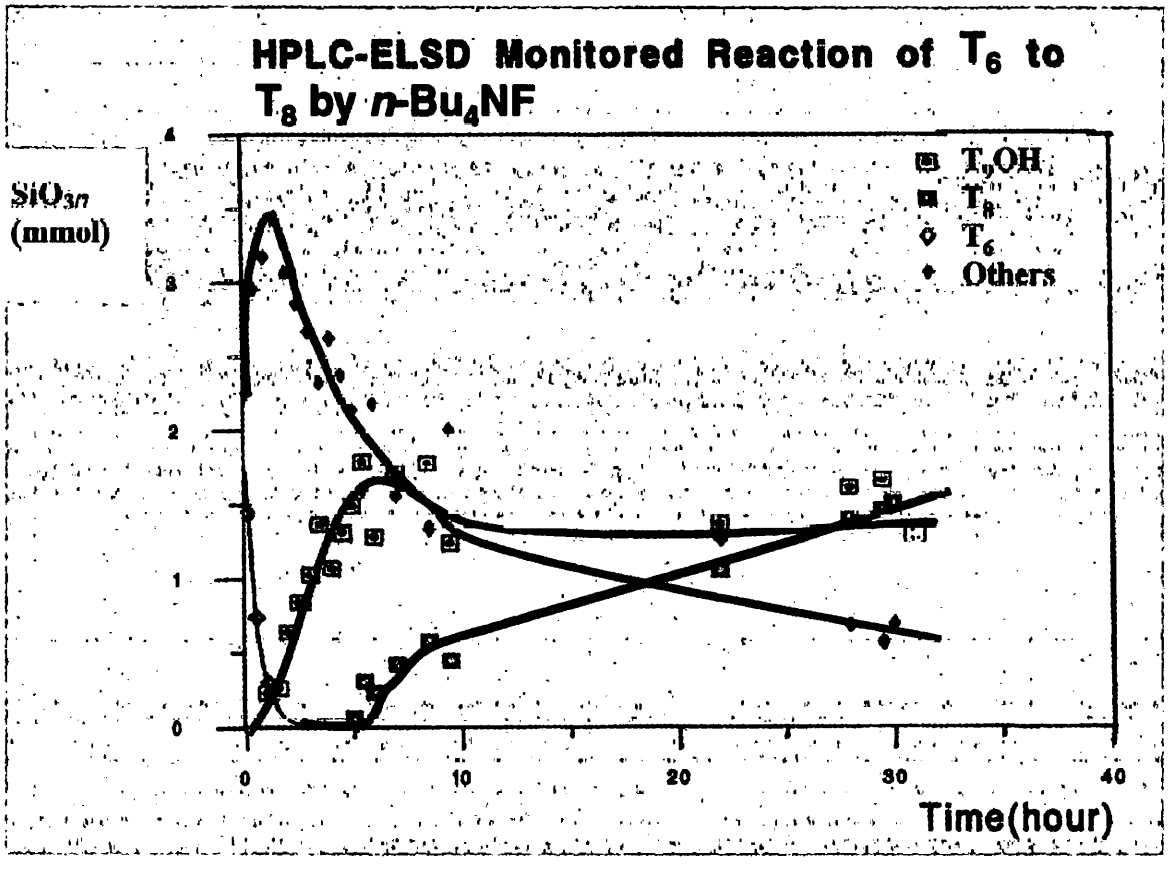
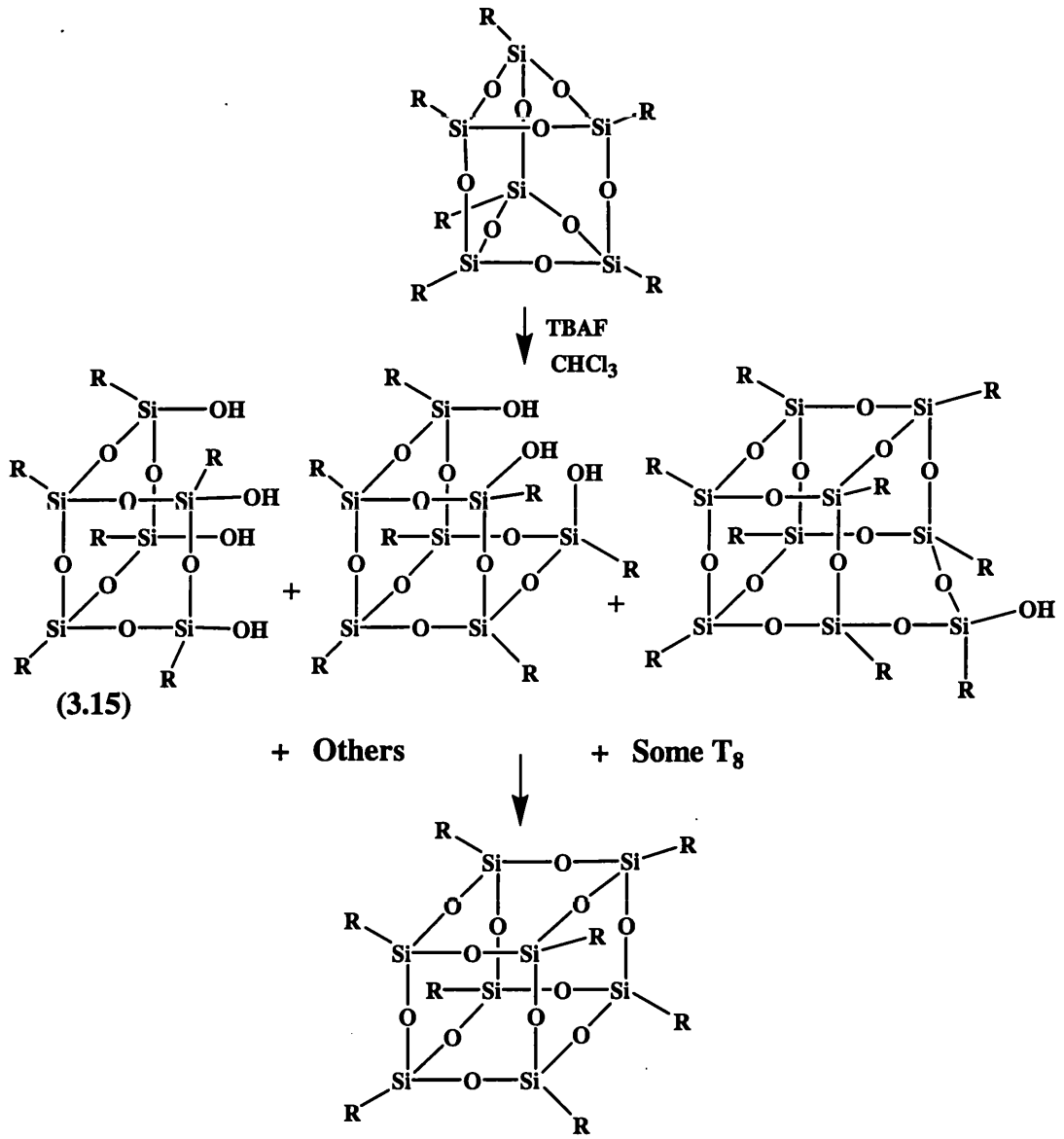


Figure 3.11

From the HPLC chromatogram, the concentration of the unknown intermediate was shown to reach a maximum after two hours, so, the reaction was repeated and stopped after 2 hours, and the reaction mixture analysed by ^{29}Si NMR. The spectra show the presence of two intermediates in the reaction mixture that could not be observed by HPLC. Fractional recrystallisation using different solvents gave the pure sample of these intermediates that

could be analysed by NMR and mass spectrometry. They were identified as the opened corner cage, $CyT_7(OH)_3$, and a ladder, $CyT_6(OH)_4$ **3.15**, as shown in Scheme 3.12.



Scheme 3.12

The reaction of CyT_9OH with TBAF was also monitored using HPLC with a silica column and 30% chloroform in hexane. The results suggested that CyT_8 was formed very early in the reaction, then builds up at the expense CyT_9OH, in agreement with the results obtained using the ^{29}Si NMR "stack experiment" of the reaction of CyT_9OH with TBAF, which the spectra were collected every 3 hours for a period of 15 hours, as shown in Figure 3.12.

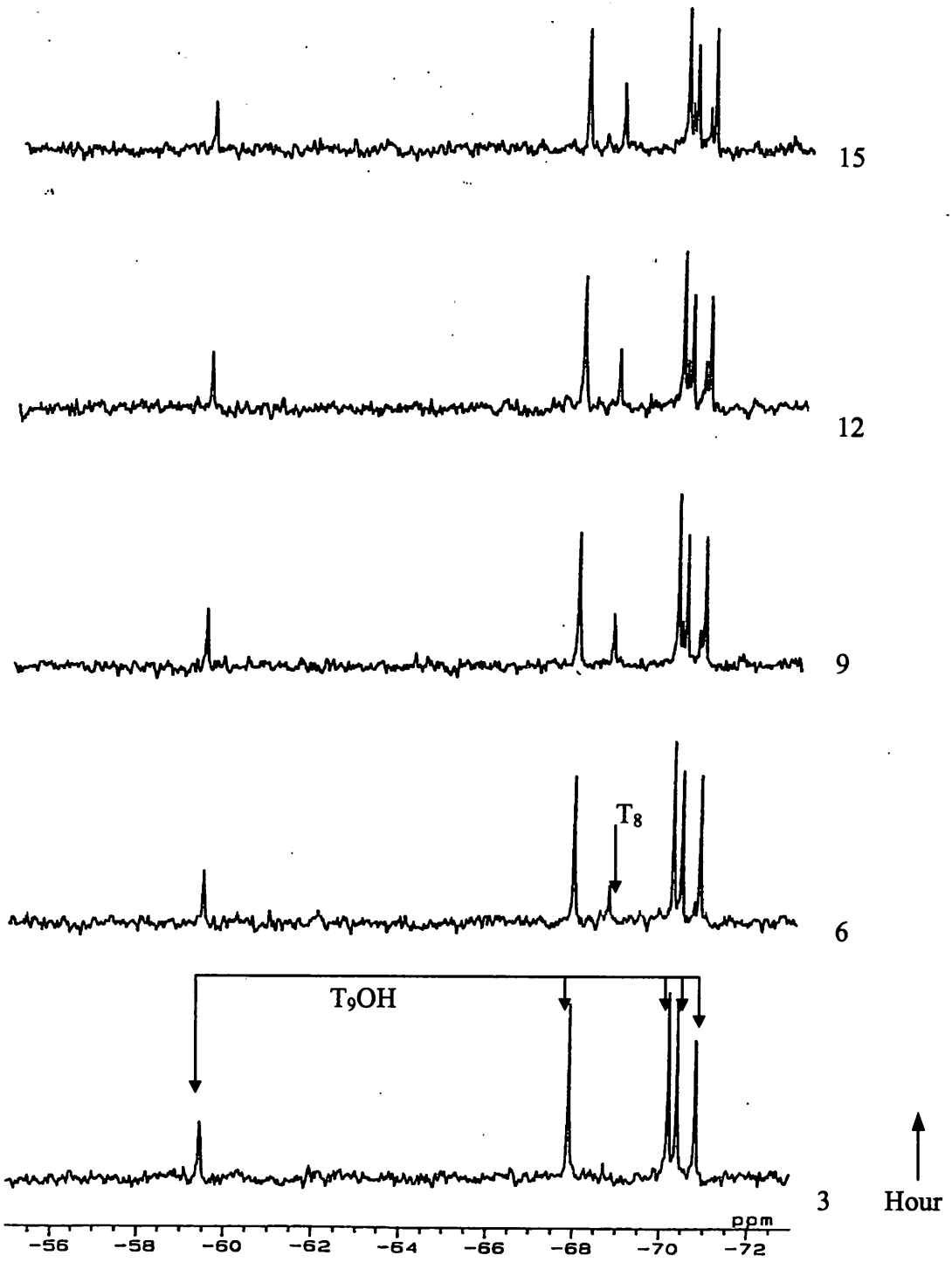


Figure 3.12

We conclude that partial cages react very quickly with TBAF to form CyT_9OH. However, in the presence of TBAF, the CyT_9OH cage undergoes further rearrangement to give the CyT_8 cage.

iii) Reaction of partial cage intermediates with TBAF

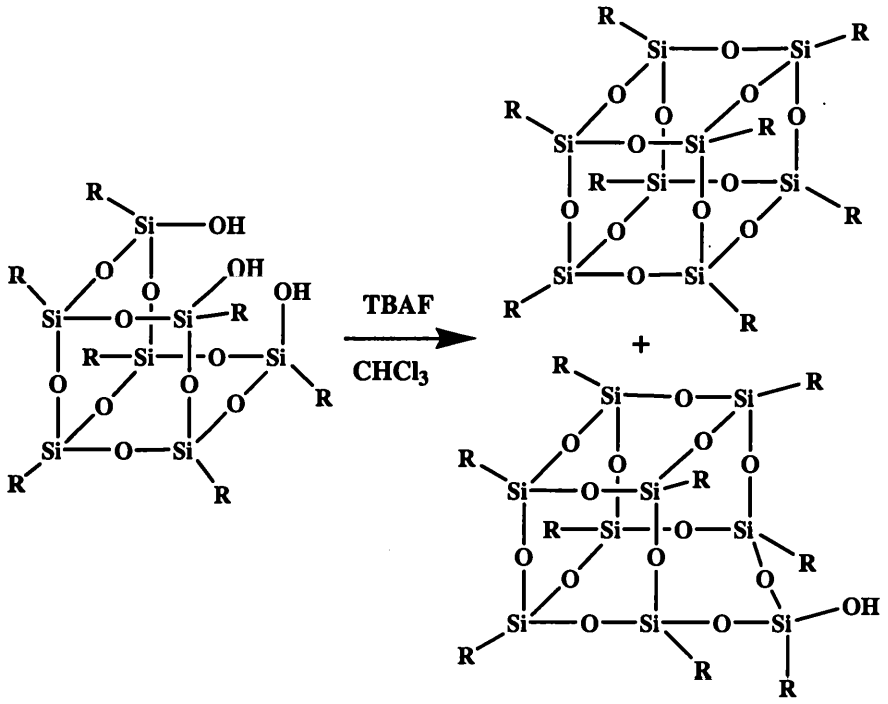
Although we had identified some of the intermediates, we could not fully understand the mechanism of the rearrangement reaction of CyT_6, to build up the higher molecular weight cage, CyT_8. Thus, the rearrangement reaction of these intermediates we identified was carried out with TBAF, in order to confirm whether these intermediates are the precursors for the formation of CyT_8.

iii-a) Rearrangement of $T_6(OH)_4$ with TBAF

Since the amount of $CyT_6(OH)_4$ **3.15** we collected was very small, thus we synthesised $CyT_6(OH)_4$ using the method of Feher and co-workers, which involved the reaction of CyT_6 with tetraethylammonium hydroxide in THF. There were two peaks in the ^{29}Si NMR for $CyT_6(OH)_4$ at -59.55 and -68.88 ppm with a ratio of 2:1. This $CyT_6(OH)_4$ was treated with 0.5 equivalents of TBAF and left overnight after which the reaction mixture was worked up as usual. A white solid gel was obtained after removal of the solvent. Extraction of the solid gel with acetone gave CyT_8, which had a single peak at -68.69 ppm in the ^{29}Si NMR. The rest of the mixture gave a rather complicated NMR pattern and so it was not possible to identify all the other high molecular weight silsesquioxanes. However, this reaction confirmed that $CyT_6(OH)_4$ was a precursor of CyT_8 in the rearrangement reaction.

iii-b) Rearrangement of $T_7(OH)_3$ with TBAF

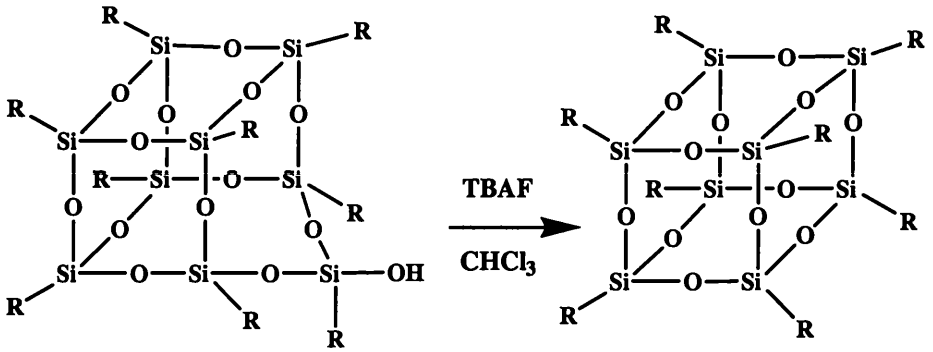
$CyT_7(OH)_3$ was obtained from the rearrangement reaction of CyT_6 with TBAF and purified by fractional recystallisation. $CyT_7(OH)_3$ was treated with TBAF and the reaction left overnight. The ^{29}Si NMR of the product showed 6 peaks appearing at -59.61, -67.92, -68.71, -70.27, -70.39 and -70.89 ppm in a ratio of 1:2:2:2:2. The peak at -68.71 ppm was from CyT_8. The remaining peaks were due to the CyT_9OH cage structure. Thus we believe that during the rearrangement process from CyT_6 to CyT_8, $CyT_7(OH)_3$ is formed before CyT_9OH, Scheme 3.13.



Scheme 3.13

iii-c) Rearrangement of CyT_9OH with TBAF

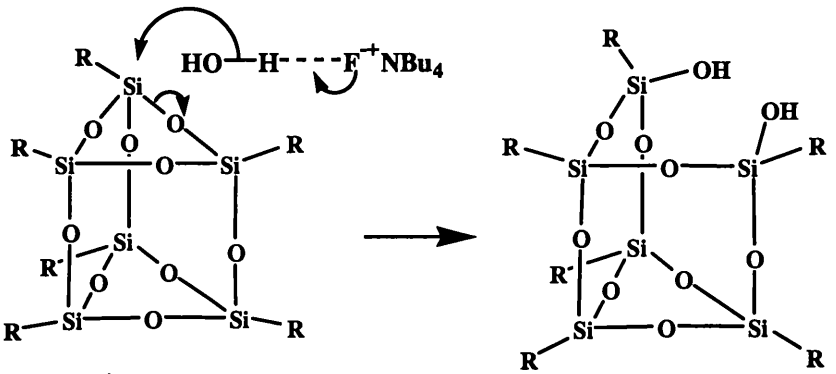
CyT_9OH was obtained from the rearrangement of CyT_6 with TBAF. CyT_9OH was treated with TBAF and the reaction left overnight. A white solid was obtained after worked up, which showed a single peak at -68.69 ppm in ^{29}Si NMR. It was identical to that obtained from CyT_8, confirming that CyT_9OH cage can be rearranged to CyT_8, as shown in Scheme 3.14.



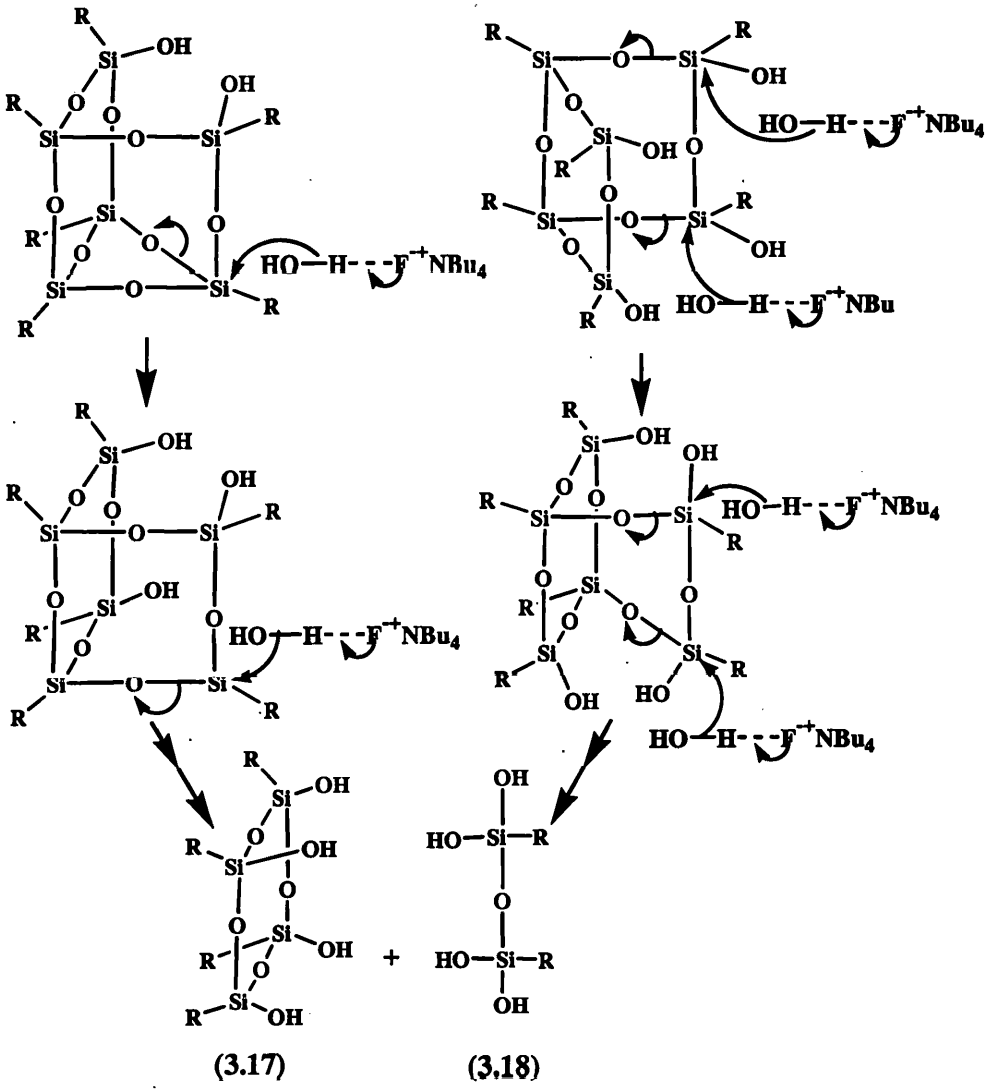
Scheme 3.14

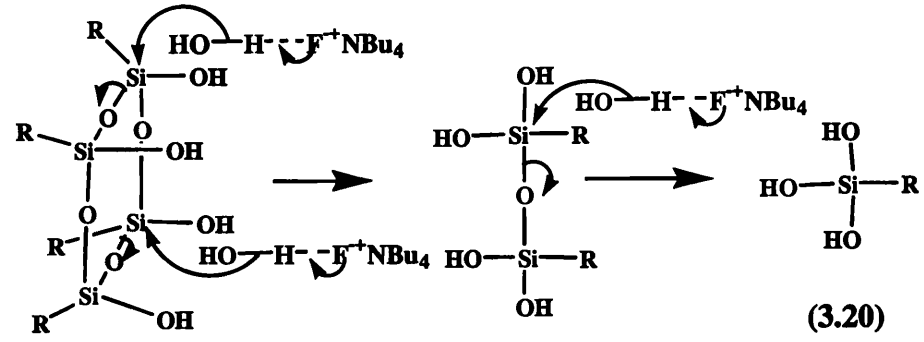
From these results, we believe the mechanism of the rearrangement reaction from CyT_6 and CyT_8 can be divided into two stages. The first stage is the degradation of CyT_6 as

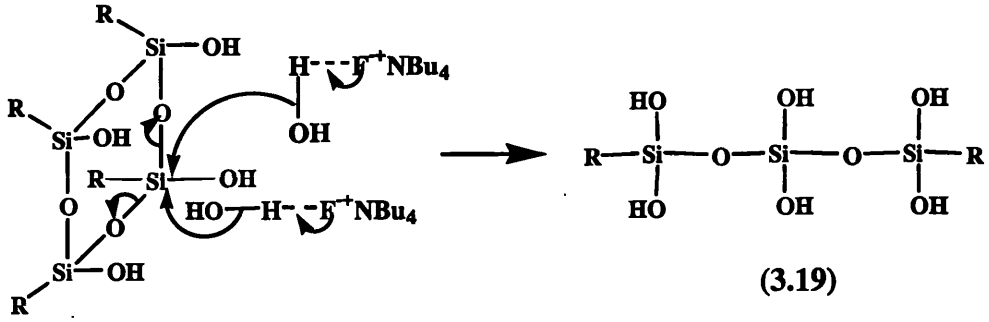
shown in Scheme 3.15, Scheme 3.16 and Scheme 3.17. Feher and co-workers reported that the cleavage of Si-OSi linkages of CyT_6 was selective, the Si-O-Si linkages of the Si-O three-membered rings, Si_3O_3, cleaving first rather than that of the Si-O four-membered rings, Si_4O_4. Thus, we proposed that the water in the TBAF solution hydrogen bonded to F^- creating a nucleophilic, OH^-, which can attack the silicon of the Si-O three-membered ring to give a diol **3.16**, as shown in Scheme 3.15. This diol then continues to break down to give tetrol **3.17** and disiloxane tetrol **3.18**. Finally a single T unit, a triol **3.19**, $CySi(OH)_3$, is produced. Of course, the tetraol also can give a trisiloxane silanol **3.20**, as shown in Scehem 3.16.



Scheme 3.15

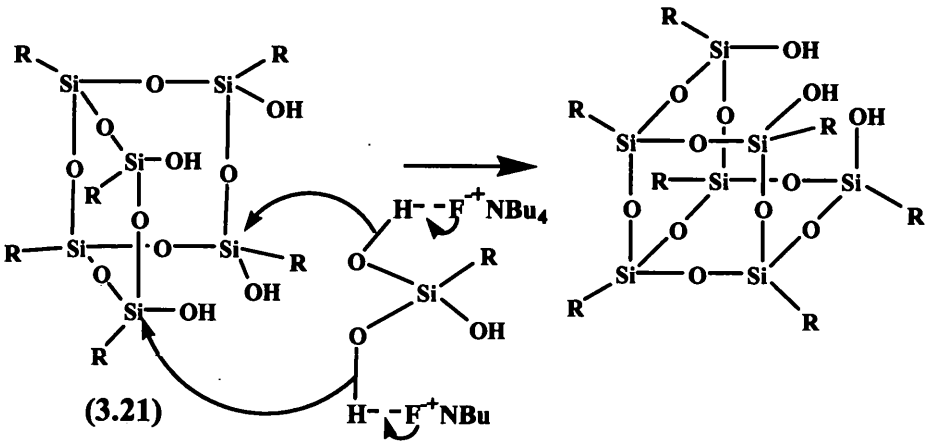






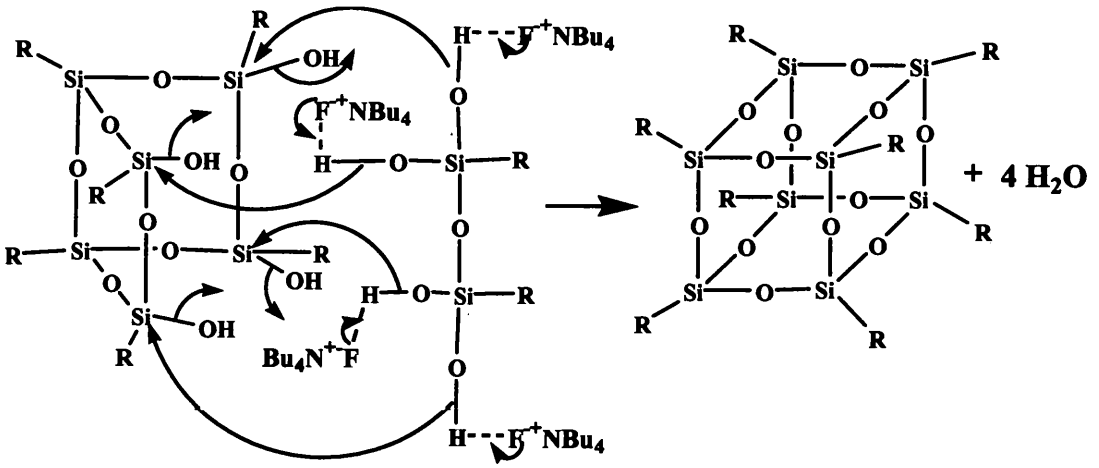
Scheme 3.16

Somehow, these species are condensed to give high molecular weight silsesquioxane cages, such as $CyT_7(OH)$, CyT_9OH and CyT_8. This occurs in the second type of the rearrangement reaction. The $CySi(OH)_3$ monomers **3.19** attack the ladder tetrol **3.21**, a $CyT_7(OH)_3$ cage is produced, as shown in Scheme 3.17.



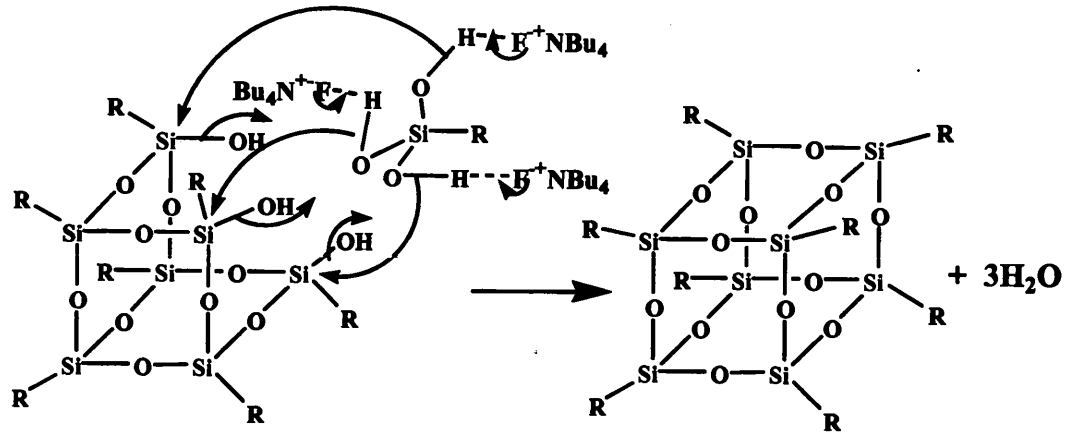
Scheme 3.17

If a disiloxane tetrol species **3.18** condenses with the ladder tetrol **3.21**, a CyT_8 cage is produced, as shown in 3.18.

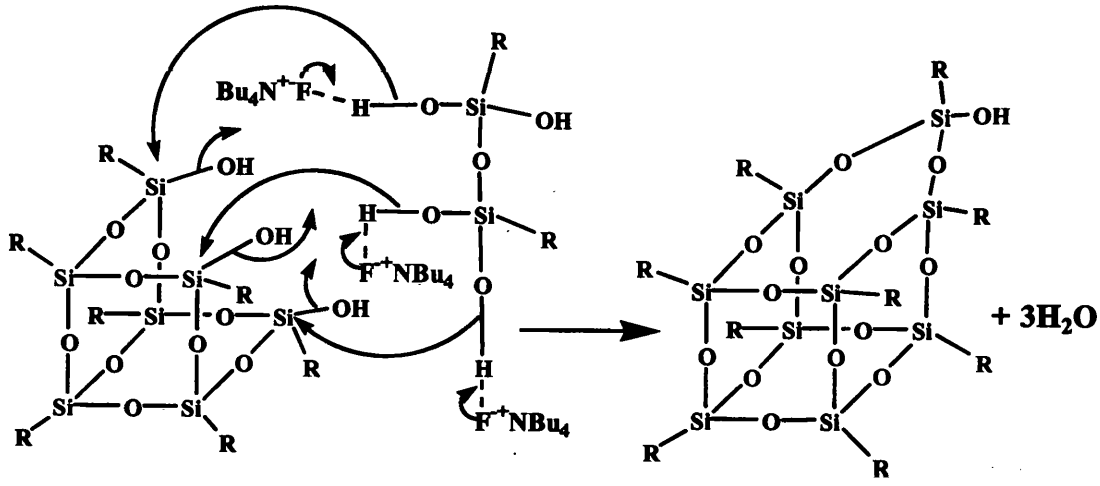


Scheme 3.18

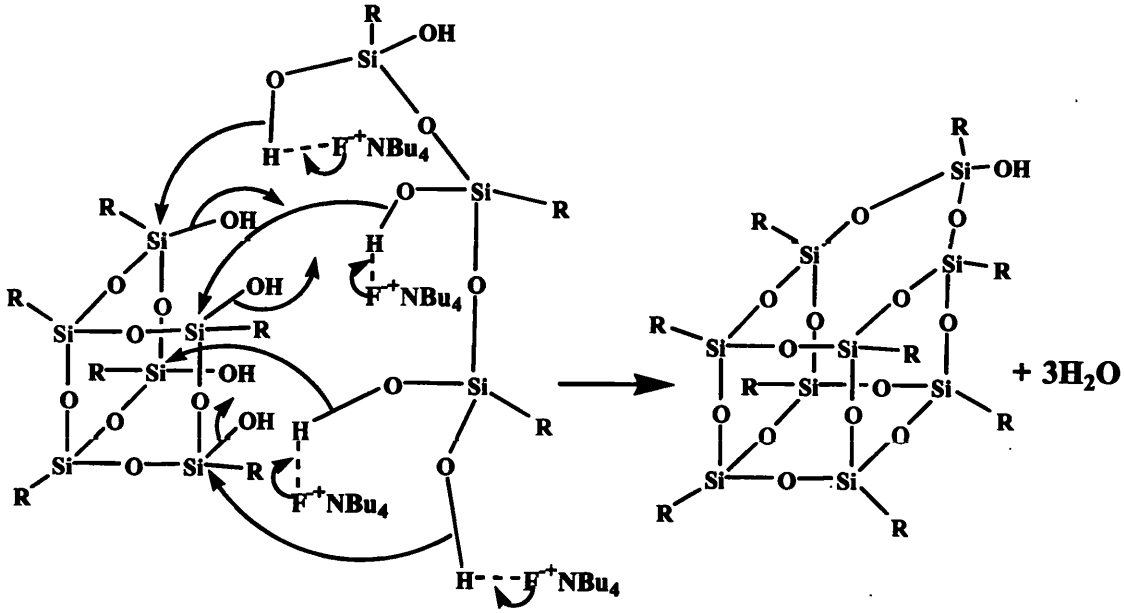
As soon as the $CyT_7(OH)_3$ was formed, condensation with other active species may continue to produce CyT_8 and $CyT_9(OH)$ cages, as shown in Scheme 3.19 and Scheme 3.20. The CyT_9OH can also be formed from the ladder tetraol **3.21** and the trisiloxane silanol **3.20**, as shown in Scheme 3.21



Scheme 3.19

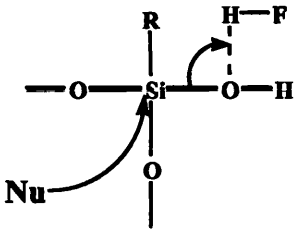


Scheme 3.20



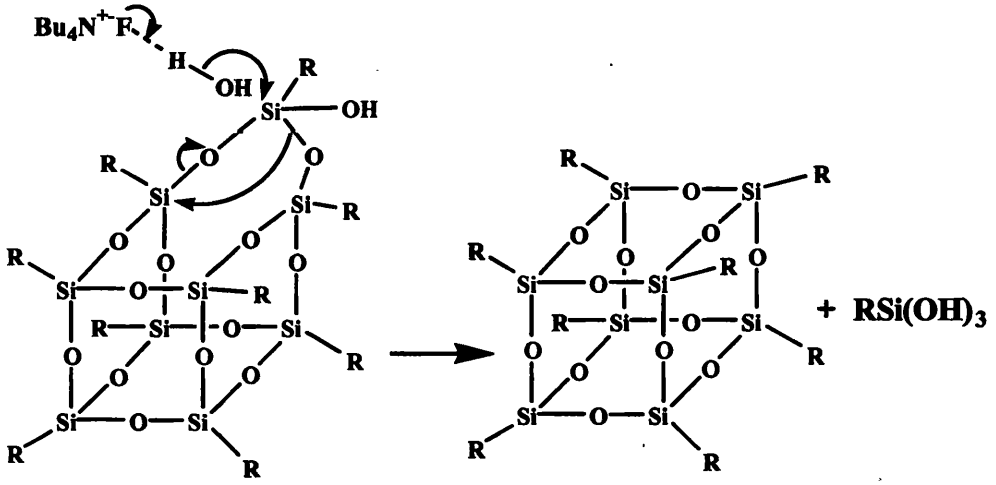
Scheme 3.21

Whilst we have drawn OH^- as the leaving group on each case, then may be aided by the HF formed as the process.



Obviously, water is reformed because of the dehydration, and this can be used again to form nucleophilic OH^- species with F^-. As with the TBAF reactions described in previous chapter, if all of the water was used, TBAF would react to form silicon fluoride adducts.

The mechanism suggests that $CyT_6(OH)_4$ and $CyT_7(OH)_3$ can be precursors of CyT_8. The NMR and HPLC also suggested that CyT_9OH was formed before CyT_8, and that CyT_9OH is subsequently rearranged to CyT_8, as shown in Scheme 3.22.


Bu4N+F-
H
OH
R
Si
OH
O
Si
R
O
Si
R
O
Si
R

believe that reaction with the water in the TBAF degrades the CyT_6 to give a opened ladder, $CyT_6(OH)_4$. The cage is built up by insertion of silicon units into the ladder to give CyT_8, together with CyT_9OH and $CyT_7(OH)_3$, which rearrange to give only CyT_8.

3.2.2 Rearrangement of Hexacyclopentylsilsesquioxane

When CpT_6, was treated with 0.5 equivalents of TBAF in chloroform, the ^{29}Si NMR "stack experiments" showed that the reaction was faster than that with CyT_6. Thus, the reaction was quenched with water after 2 hours in order to identify any intermediates. The product mixture was separated by fractional recrystallisation to give triol, $CpT_7(OH)_3$, CpT_9OH, CpT_8 and ladder tetraol, $CpT_6(OH)_4$ as the major products. They were all characterised by ^{29}Si NMR and mass spectrometry. Therefore CpT_6 follows a similar pathway to CpT_6, involving rearrangement to a higher molecular weight cage via partial cages, such as $CpT_6(OH)_4$, $CpT_7(OH)_3$ and CpT_9OH.

3.2.3 Rearrangement of Hexa-iso-butylsilsesquioxane

Iso-butylT_6 was treated with 0.5 equivalents of TBAF in chloroform and the reaction stopped after two hours by washing with water. After removal of the solvent the residue was separated using chromatography. Two products were obtained, *iso*-butylT_8 as a crystalline solid in 39.2% yield and *iso*-butylT_9OH as an oily gel. Attempts to monitor the reaction using HPLC failed because the reaction was very fast and each injection needed about 30 minutes, so very little information could be obtained on the early part of the reaction. However, the *iso*-butylT_9OH cage could be obtained as an oily product by stopping the reaction at 2 hours and then separating on a silica-gel column with hexane as the eluents.

3.2.4 Rearrangement of Hexaoctylsilsesquioxane

OctylT_6 was treated with 0.5 equivalents of TBAF in chloroform and the reaction was stopped after two hours by washing with water. After removal of the solvent, an oily

residue was obtained. ^{29}Si NMR showed that OctylT_8 was produced along with a tiny amount of other adducts appearing between -67 and -68 ppm. OctylT_8 was not isolated from the mixture because the starting material, OctylT_6, could only be obtained in small amounts so that the rearrangement only started with very small amount of OctylT_6, and led to a tiny amount of product. From the NMR, OctylT_8 was obtained in 70% yield.

3.2.5 Rearrangement of Hexa-p-methoxyphenylpropylsilsesquioxane

p-MethoxyphenylpropylT_6 was treated with 0.5 equivalents of TBAF as before. However, the reaction was left only for 1 hour, because the linear arm on the core is more flexible leading to a faster rearrangement reaction. After 1 hour, the reaction mixture was worked up in the usual way, and gave a white solid with some oily product after removal of solvent. ^{29}Si NMR of this mixture showed *p*-methoxyphenylpropylT_8 and *p*-methoxyphenylpropylT_9OH cage was produced with a very small amount of starting material. *p*-methoxyphenylpropylT_8 was isolated as a cubic crystal in 29.2% yield from the mixture by recrystallisation in hexane and chloroform (3:1), but *p*-methoxyphenylpropylT_9OH could not be further purified.

X-ray crystallographic analysis showed that *p*-methoxyphenylpropylT_8 is built from 2 Si-O four-membered rings, Figure 3.13. The average Si-O bond length is 1.615 Å and the Si-O-Si bond angles were 149.59°. The average O-Si-O bond angles were 108.81°, similar to other T_8R_8 cages (O-Si-O: 108°). Comparing with the corresponding *p*-methoxyphenylpropylT_6, the Si-O the bond lengths and the Si-O-Si bond angles are very similar, but the Si-O-Si bond angles of the *p*-methoxyphenylpropylT_8 are nearly 10° different from that of the Si-O four-membered ring of *p*-methoxyphenylpropylT_6 (average Si-O-Si bond angle of the Si-O four-membered ring of T_6: 140.04°). These results show that the different ring strain clearly affects the Si-O-Si bond angles. Again, the *p*-methoxyphenylpropyl groups on the core are lined on planes. The phenyl rings are

orthogonal to the cage. There are four phenyl groups on each side that pack to form a square.

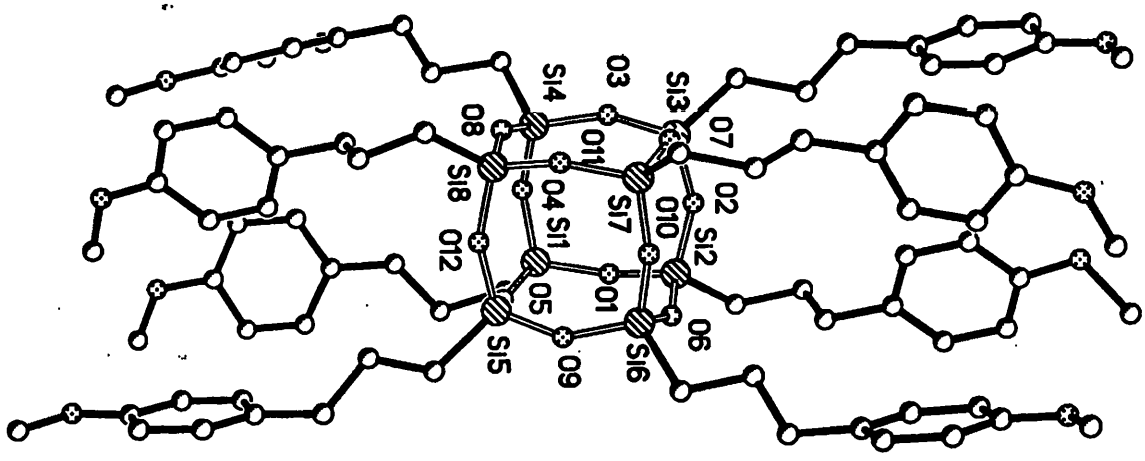


Figure 3.13

Table 3.5 summarises the bond lengths and the bond angles in *p*-methoxyphenylpropylT_6 and *p*-methoxyphenylpropylT_8.

Table 3.5 Comparison of bond length and angles of T_6 and T_8 with *p*-methoxyphenylpropyl groups on the core

Si-O Four-member ring of	Si-O (Å)	Si-O-Si	O-Si-O (Å)
T_6	1.626	140.05	107.37
T_8	1.615	149.59	108.81

In summary, T_6R_6 with R groups on the core, R = cyclohexyl, cyclopentyl, *iso*-butyl, octyl, and *p*-methoxyphenylpropyl, can be rearranged with a variety of catalysts, to give higher molecular weight cages and eventually the T_8R_8 cage as the most stable species. A mechanism of the rearrangement reaction has been proposed, based on the experimental observations. The yield of the rearrangement reactions is summarised in Table 3.6.

Table 3.6 Comparison of the ^{29}Si NMR of T_6R_6 and T_8R_8 and the yield of T_8R_8 from the rearrangement of T_6R_6

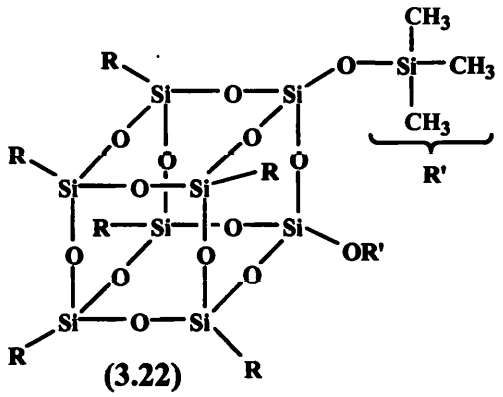
R	T_6 δ (ppm)	T_8 δ (ppm)	Yield of T_8 (%)
Cy	-56.60	-68.69	34.7
Cp	-54.36	-66.57	22.9
Iso-butyl	-55.43	-66.55	39.2
*Octyl	-54.18	-66.63	70*
p-methoxyphenylpropyl	-54.42	-66.76	29.2

*Calculated by NMR.

3.3. Rearrangement of Hexasilsesquioxanes using TBAF in the presence of Spherosilicate Cages

In the previous section, we demonstrated that the rearrangement of T_6R_6 to T_8R_8 by TBAF involves a number of opened partial cage intermediates, that can insert in the opened ladder, $CyT_6(OH)_4$. Since Q_8R_8 breaks down rapidly under the influence of TBAF to give M_4Q units, it is possible that the Q fragment may be inserted into the open silsesquioxane cage prior to formation of T_8R_8. Thus a mixture of T_6R_6 and Q_6R_6/Q_8R_6 was treated with TBAF.

In fact, a variety of T_6R_6 and Q_8R_8 cages were employed in these insertion reactions, such as CyT_6, CpT_6, $OctT_6$, *iso*-butylT_6, Q_6^M, Q_8^M, Q_8^V, and Q_8^H. In each case an octahedral cage is formed which contain 6 T units and 2 Q units **3.22**, as discussed below.

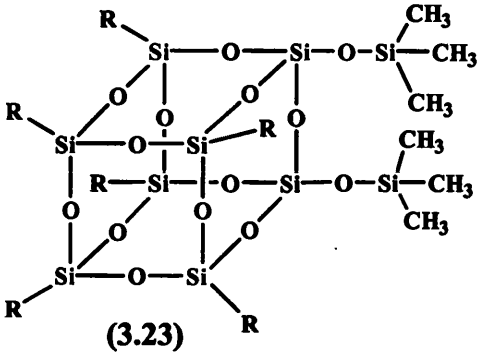


(3.22)

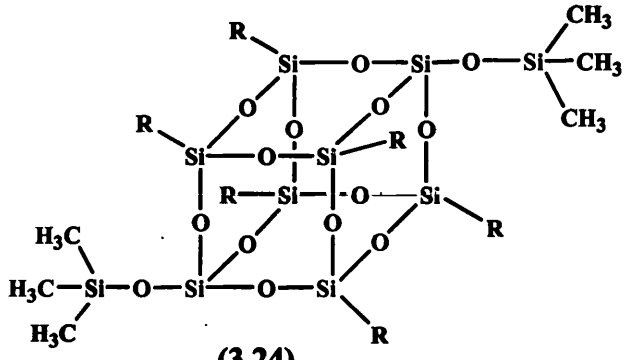
3.3.1 In the Presence of Q_6^M/Q_8^M

3.3.1.1 Rearrangement of Hexacyclohexylsilsesquioxane in the Presence of Q_6^M

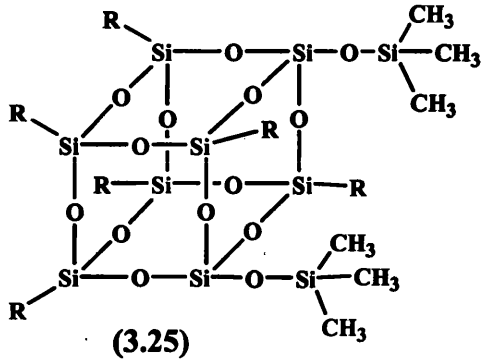
The rearrangement reaction of CyT_6, with TBAF in the presence of Q_6^M was carried out as follows: a solution CyT_6 and Q_6^M in chloroform was stirred overnight with 0.5 equivalents of TBAF. The mixture was then extracted with water. After separation of the organic layer and removal of the solvent, a solid gel residue was obtained. This residue was extracted with acetone to give a white solid product, which gave four peaks in the ^{29}Si NMR at 11.45, -68.05, -68.62, and -108.28 ppm in a ratio of 1:2:1:1, as shown in Figure 3.14. This corresponds to an octahedral cage structure, which contains 6 T units and 2 Q units. MALDI-TOF mass spectrometry confirmed this assignment, as shown in figure 3.16. There are three possible $CyT_6Q_2^M$ structures, such as **3.23**, **3.24** and **3.25**.



(3.23)



(3.24)



(3.25)

In ^{29}Si NMR, the symmetry of the cage suggests **3.23** will give arising 3 peaks with a ratio of 1:2:1, and **3.24** will give arising 2 peaks in ratio of 3:1 and **3.25** will give arising 4 peaks in a ratio of 1:1:1:1. Figure 3.1 shows a peak at 11.45 ppm corresponding to the OTMS

group and three peaks in a ratio of about 2:1:1 suggested the most likely arrangement is the "*ortho*" compound.

Recrystallisation from hexane gave regular cubic crystals. However, we were unable to obtain an X-ray crystal structure because disorder within the crystal. We tried to recrystallise this product from a different solvent system and even at different temperatures, but the X-ray crystallographic analysis was always unsuccessful using the EPSRC service in Southampton. Subsequently, the crystal was analysed at low temperature using an instrument in Berlin. The crystal structure was obtained, as shown in Figure 3.16. It clearly shows the cubic cage, but because of the symmetry of the cubic cage, the OTMS ligand did not pack in consistent position so that the arms were not well resolved and we could not differentiate between structure **3.23**, **3.24** and **3.25**.

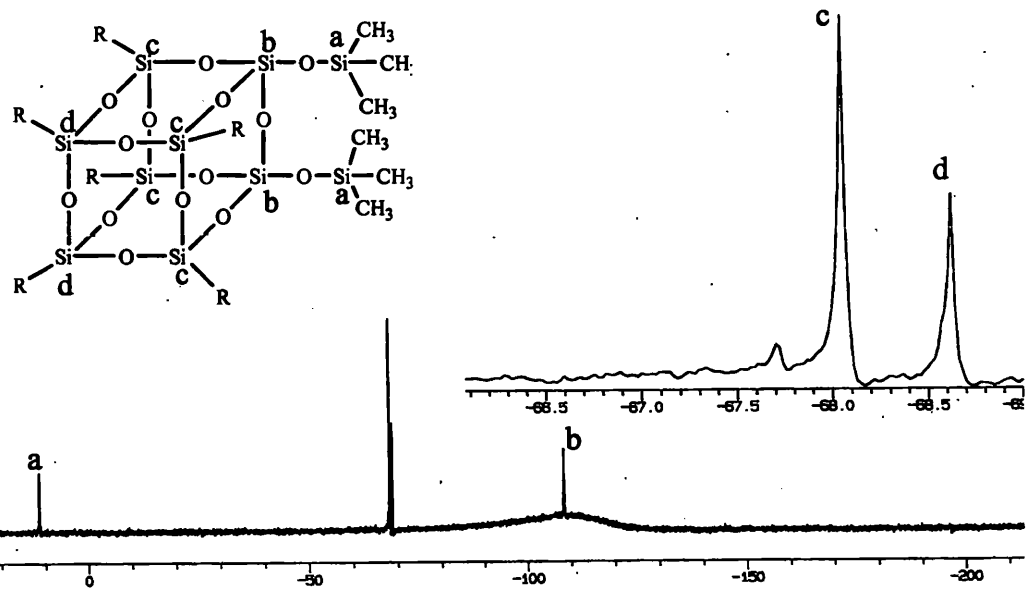


Figure 3.14

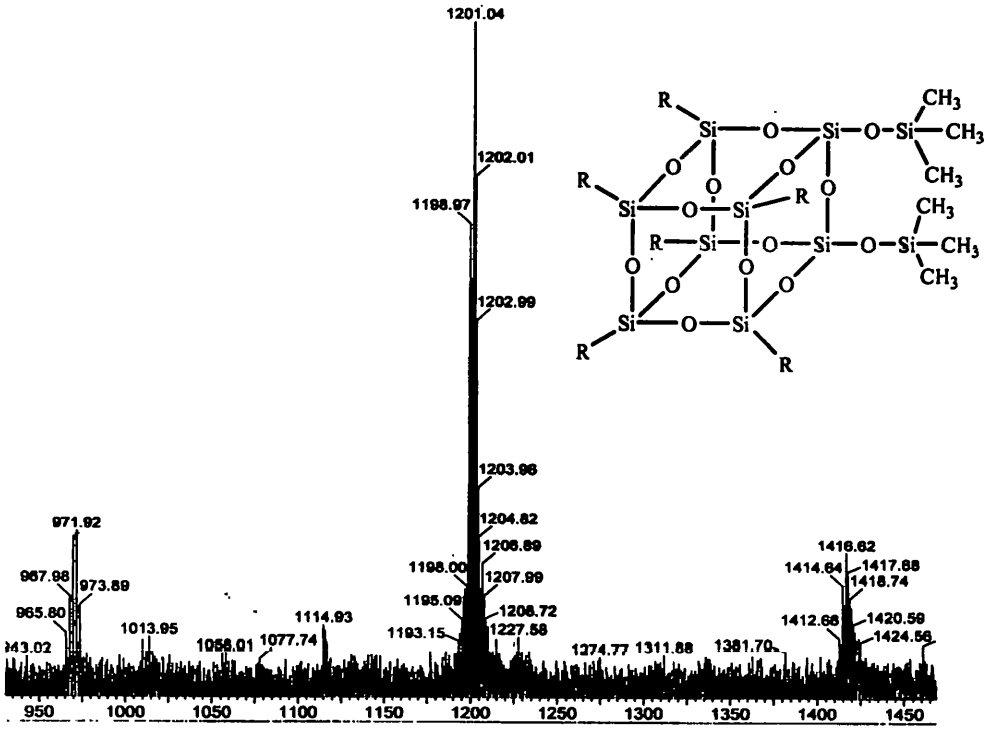


Figure 3.15

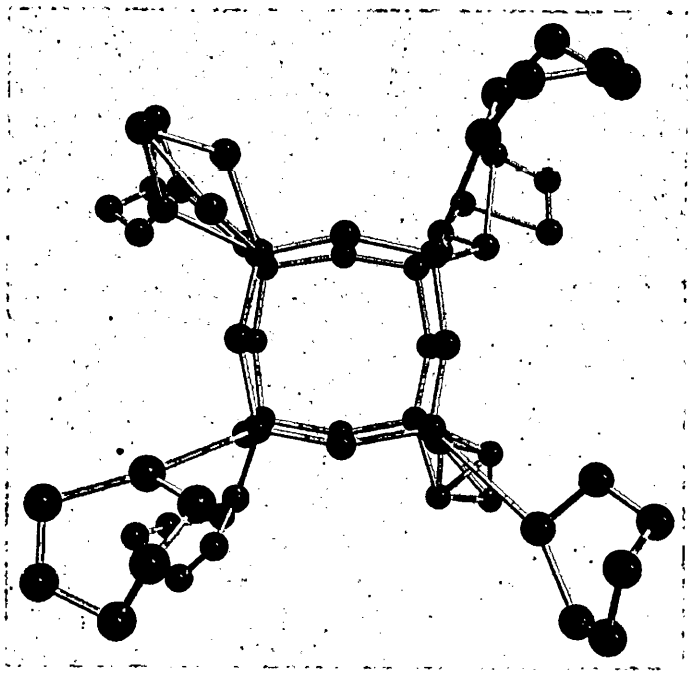
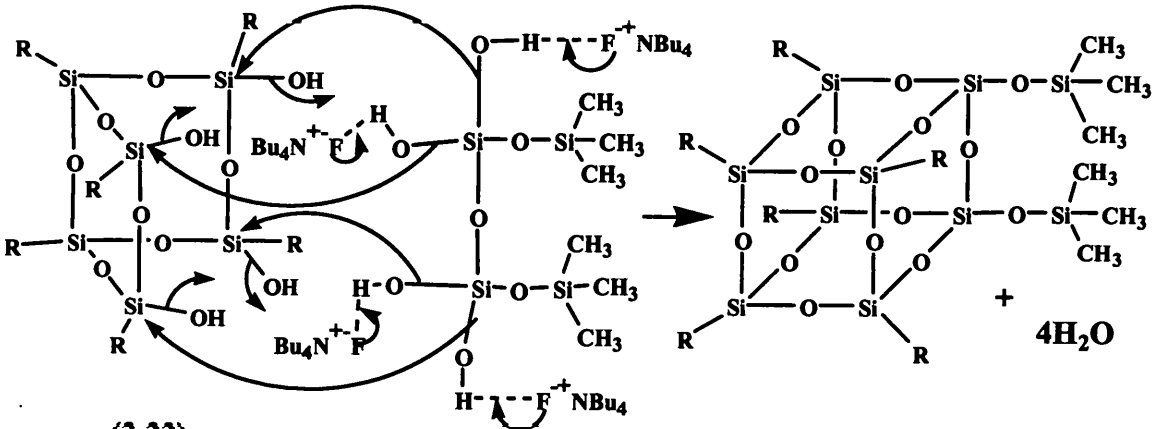


Figure 3.16

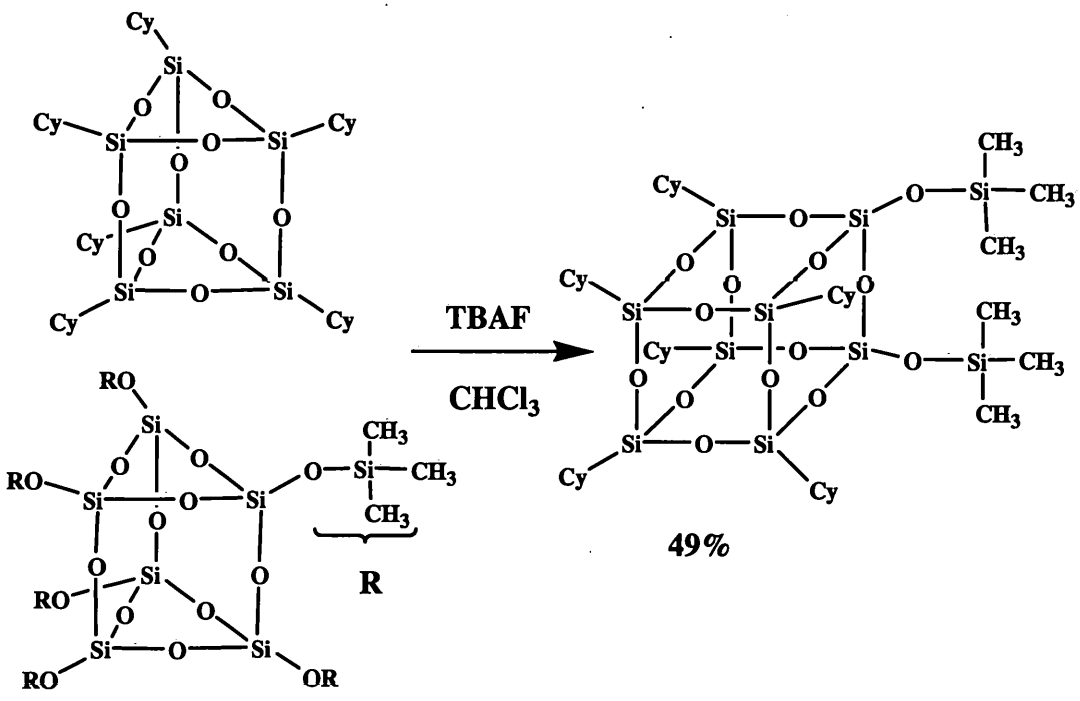
The formation of $CyT_6Q_2^M$ suggests that the Q_6^M is degraded as described earlier to give disiloxane Q units and single Q units. This is in agreement with earlier studies that show

that Q_6^M/Q_8^M cages were degraded very rapidly. Thus, CyT_6 degradation gave a ladder tetrol structure $CyT_6(OH)_4$, and insertion of disiloxane Q unit **3.26** into this ladder tetrol **3.22** forms the closed cage structure $CyT_6Q_2^M$, as shown in Scheme 3.23.



Scheme 3.23

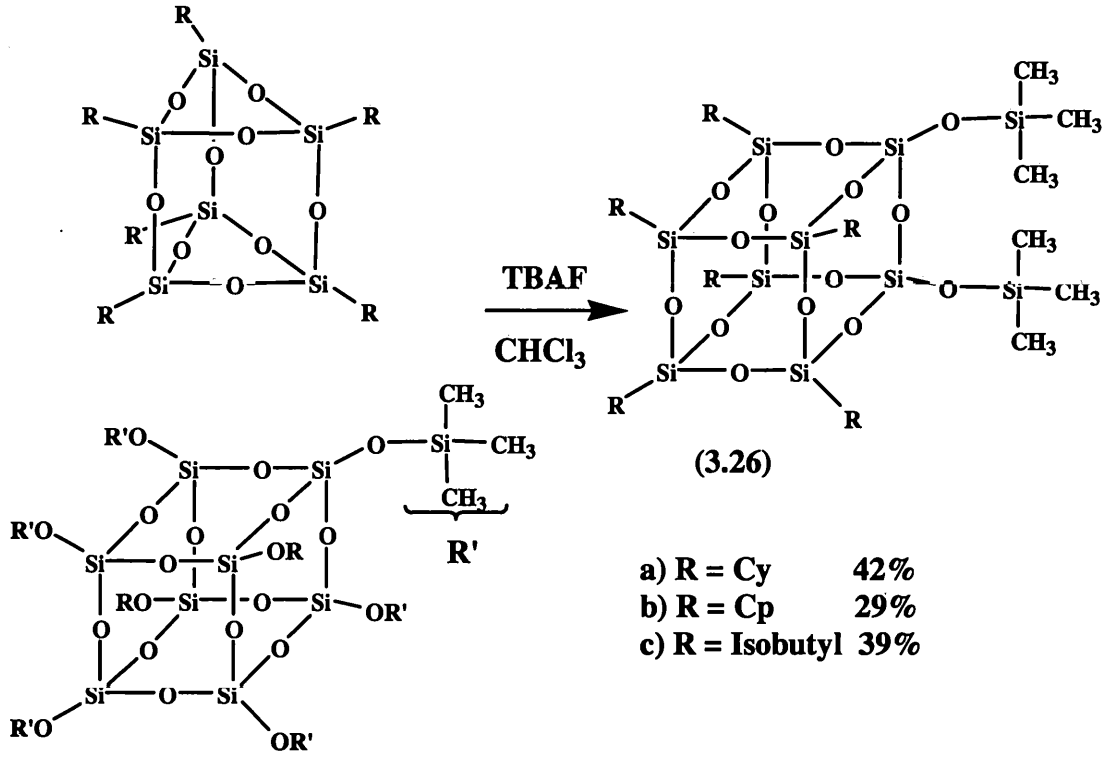
To optimise the reaction conditions, we examined two variables, the ratio of CyT_6 to Q_6^M and the amount of TBAF. It had been demonstrated that a 0.5 equivalents of TBAF is the optimum amount for the rearrangement of CyT_6 and this was the quantity used in further reactions. To determine the optimum CyT_6 to Q_6^M ratio, the reaction was carried out at a mole ratio of 1:0.5, 1:1 and 1:2 of CyT_6:Q_6^M. No $CyT_6Q_2^M$ cage was observed when the 1:0.5 molar ratio was employed. $CyT_6Q_2^M$ cage was formed in both of the other reactions. However, the yield in the reaction, which used a ratio of 1:2 was higher than that obtained when the ratio was 1:1. However, this does not mean that the higher the ratio of Q_6^M the higher the yield of $CyT_6Q_2^M$ cage, since there was only a certain amount of TBAF (0.5 equivalents) this would be consumed in the break down of the Q_6^M cage. Thus, too much Q_6^M would lead to resin formation, which would complicate isolation of the $CyT_6Q_2^M$ and reduced the breakdown of the CyT_6. Therefore, we decided that the optimum conditions for the formation of $CyT_6Q_2^M$ is to use 0.5 equivalents of TBAF in a ratio 1:2 of CyT_6 to Q_6^M, Scheme 3.24.



Scheme 3.24

b) Rearrangement of Hexacyclohexylsilsesquioxane in the Presence of Q_8^M

The reaction of hexacyclohexylsilsesquioxane, CyT_6, with TBAF in the presence of Q_8^M was carried out using similar procedure to that of Q_6^M. Thus, a solution of CyT_6, and Q_8^M in chloroform was stirred overnight with 0.5 equivalent of TBAF and then the mixture was washed with water, as shown in Scheme 3.25.



Scheme 3.25

After separation of the organic layer and removal of the solvent, a white solid gel residue was obtained. This residue was extracted with acetone to give a white solid product, which gave four single peaks in the ^{29}Si NMR at 11.45, -68.05, -68.62, and -108.28 ppm in a ration of 1:2:1:1. The spectra suggested that this was the same product as that obtained from a mixture of Q_6^M and CyT_6. MALDI-TOF mass spectroscopy confirmed that the product was a $CyT_6Q_2^M$ cage **3.25a** in 41.8% yield, containing 6 T units and 2 Q units. Again X-ray Crystallography was used to confirm the structure of the cage. Unfortunately, again which cage was clearly present and the arrangement of the arms could not be solved.

A series of reactions with different ratios of CyT_6 to Q_8^M (1:0.5, 1:1 and 1:2) was carried out with 0.5 equivalent TBAF to determine the optimum conditions for the formation of $CyT_6Q_2^M$ cage. The results were similar to those obtained with Q_6^M. The optimum condition was to use CyT_6 and Q_8^M in a ratio of 1:2 with 0.5 equivalents TBAF.

3.3.1.2 Rearrangement of Hexacyclopentylsilsesquioxane in the Presence of Q_8^M

Although the rearrangement of CpT_6, with TBAF was faster than the rearrangement of CyT_6, the reaction of CpT_6 in the presence of Q_8^M was carried out using the same conditions as those employed with CyT_6. Thus, a mixture in a ratio of 1:2 CpT_6 and Q_8^M in chloroform was stirred overnight with 0.5 equivalent of TBAF. After removal of the solvent and extraction with acetone, a product was obtained which gave ^{29}Si NMR peaks at 11.63, -65.98, -66.50, and -108.24 ppm in a ration of 1:2:1:1. The spectra confirm that a similar $CpT_6Q_2^M$ cage **3.25b** was obtained in 29.0% yield. This was confirmed by MALDI-TOF mass spectrometry, which showed a peak at *m/z* 1032 ($M+Na^+$).

3.2.1.3 Rearrangement of Hexa-iso-butylsilsesquioxane in the Presence of Q_8^M

Iso-butylT_8 had been shown to form a good crystalline solid, and we hoped that the corresponding T_6Q_2 would also crystallise readily from the mixture. Thus, a solution of *iso*-butylT_6 and Q_8M_8 in a ratio of 1:2 in chloroform was stirred overnight with 0.5 equivalents of TBAF. After removal of the solvent and washing with acetone, a product was obtained which gave ^{29}Si NMR peaks at 11.37, -67.03, -67.86, and -108.39 ppm in a ratio of 1:2:1:1. The spectra suggested that a similar *iso*-butyl$T_6Q_2^M$ cage **3.25c** had been obtained. This was confirmed by MALDI-TOF mass spectrometry, *m/z* 1045.16. However, the yield was relatively low and it was again impossible to determine its structure by X-ray crystallography.

3.2.1.4 Rearrangement of Hexaoctylsilsesquioxane in the Presence of Q_8^M

A solution of OctylT_6, and Q_8^M in a ratio of 1:2 in chloroform was stirred overnight with 0.5 equivalents of TBAF. After removal of the solvent and washing with acetone, an oily product was obtained which showed two sharp peaks in the ^{29}Si NMR at -66 and -67 ppm along with a great deal of resin in the region of -65 and 11 ppm. Attempts to separate the mixture failed since the oily product did not dissolve in any solvents apart from chloroform. Chromatography was employed, but nothing eluted from the column. It was

clear that this reaction had formed mainly resin, which could not be separated from the product. The pattern of peaks indicated that Octyl$T_6Q_2^M$ cage formation had not been successful, however, it was possible that an OctylT_7Q^M cage had been formed. Unfortunately, we could not confirm the presence of the OctylT_7Q^M cage in the mixture since MALDI-TOF mass spectroscopy failed for this mixture.

3.2.1.5 Rearrangement of Hexa-p-methoxyphenylpropylsilsesquioxane in the Presence of Q_8^M

Despite the *p*-methoxyphenylpropyl group involving a linear carbon chain, the *p*-methoxyphenylpropylT_8 is a good crystalline solid mainly because of packing of the phenyl groups. Thus we hoped that the *p*-methoxyphenylpropyl$T_6Q_2^M$ cage would be easy to isolate by recrystallisation. Thus, a solution of *p*-methoxyphenylpropylT_6 and Q_8^M in a ratio of 1:2 in chloroform was stirred overnight with 0.5 equivalents of TBAF. After removal of the solvent and washing with acetone, an oily product was obtained which showed two sharp peaks in the ^{29}Si NMR at -66.60 and -66.76 ppm although a good deal of resin was also seen between -65 to -68 ppm and a region of 11 ppm. Attempts to separate the reaction mixture using recrysatllisation and chromatography failed because the oily product did not dissolve in any solvents apart from chloroform . Although one of the peaks at -66.60 ppm could arise from the *p*-methoxyphenylpropylT_8, it was not possible to assign any of the other peaks.

In summary, $R_6T_6Q_2R'_2$ cages could be synthesised by the rearrangement of the corresponding T_6R_6 with TBAF in the presence of Q_6^M/Q_8^M. The preparation seemed to work best when the T_6R_6 contained relatively bulky groups on the core and the yields suggest an order of ease of formation:

Cyclohexyl >Cyclopentyl>Isobutyl>*p-Methoxyphenylpropyl* ≈ Octyl

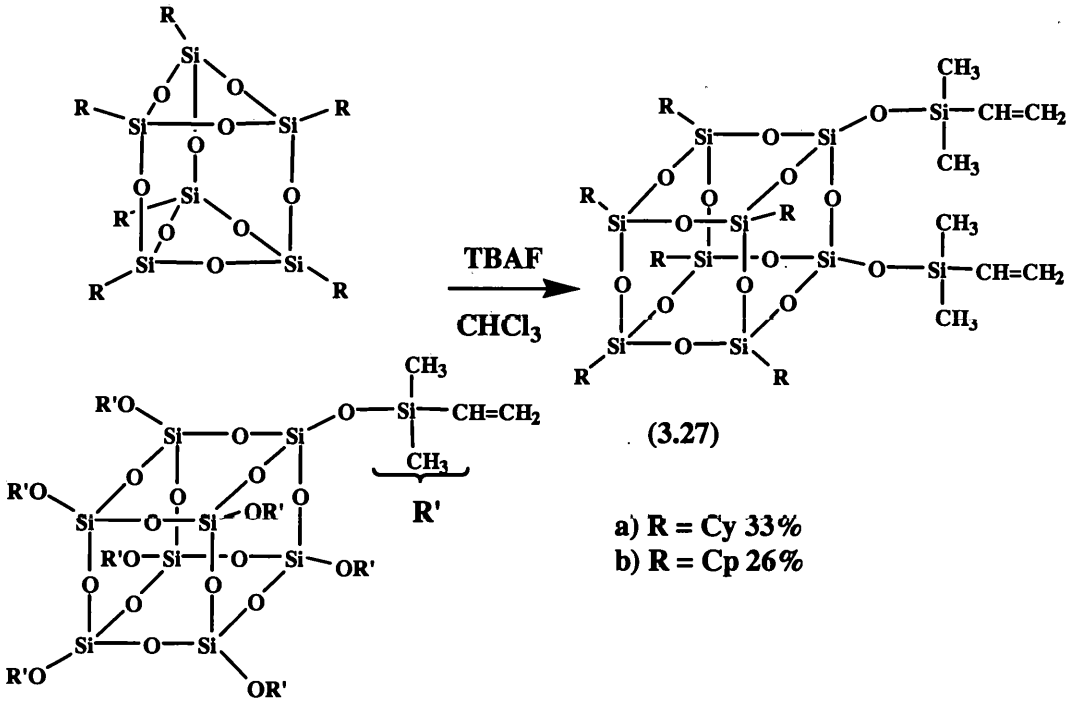
3.3.2 Rearrangement of hexasilsesquioxanes in the presence of Q_8^V

To expand the range of $R_6T_6Q_2R_2$ compounds, Q_8^V cage was employed. Q_8^V was chosen mainly because it was easy to prepare in high yields. Since the reaction of *p*-methoxyphenylpropylT_6 and octylT_6 with TBAF in the presence of Q_8^M had not been very successful, and because the *iso*-butylT_6 was not easy to purify from the DMSO reaction, these substrates were not selected for reaction with TBAF in the presence of Q_8^V. Thus, we only examined the rearrangement reaction of CyT_6 and CpT_6.

3.3.2.1 Rearrangement of Hexacyclohexylsilsesquioxane in the presence of Q_8^V

The reaction of CyT_6 with TBAF in the presence of Q_8^V was carried out using the same conditions as were used with Q_8^M. Thus, a solution of CyT_6 and Q_8^V in a ratio of 1:2 in chloroform was stirred overnight with 0.5 equivalent of TBAF, Scheme 3.26.

After removal of the solvent and washing with acetone, a product was obtained which gave ^{29}Si NMR peaks at -0.53, -68.03, -68.62 and -108.39 ppm in a ratio of 1:2:1:1. The spectra again suggest a $CyT_6Q_2^V$ structure, compound **3.27**, which was confirmed by MALDI-TOF mass spectrometry.

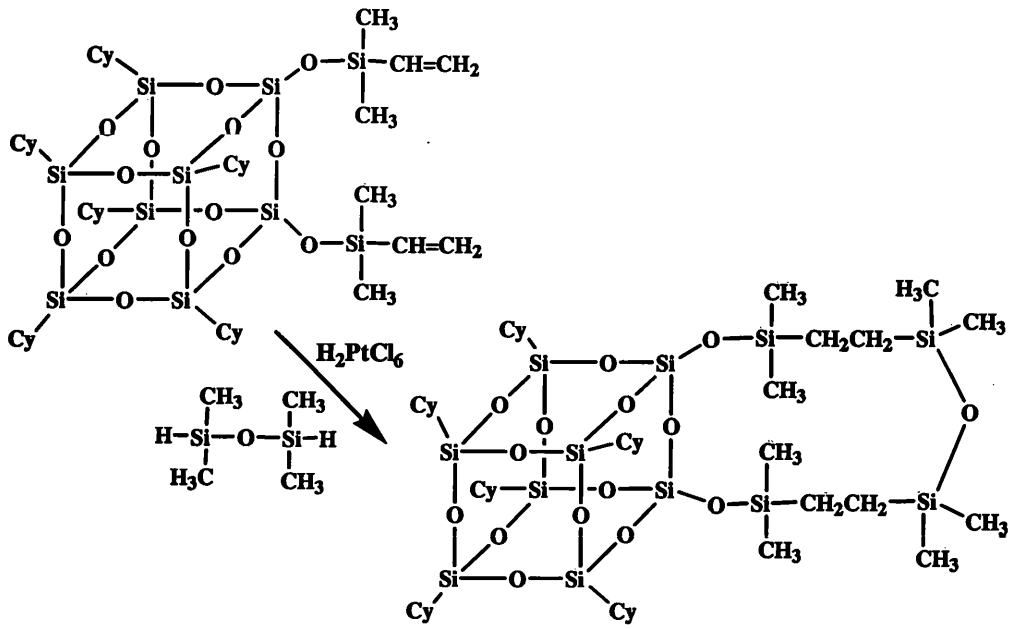


Scheme 3.26

To confirm that two -$OSiMe_2CH{=}CH_2$ units were attached to the core, this $CyT_6Q_2^V$ cage, hydrosilylation of $CyT_6Q_2^V$ was also carried out using tetramethyldisiloxane, $HMe_2SiOSiMe_2H$. The ^{29}Si NMR showed two new peaks, apart from the cage. MALDI-TOF mass spectroscopy suggested the formation of a single product, compound **3.28**, with a *m/z*, of 1359 ($M+Ag^+$), as shown in Scheme 3.27.

This strongly suggests that the two Q vinyl groups are next to each other (*ortho*), since it would not be possible to cyclise, if the Q groups were " *meta*" or "*para*".

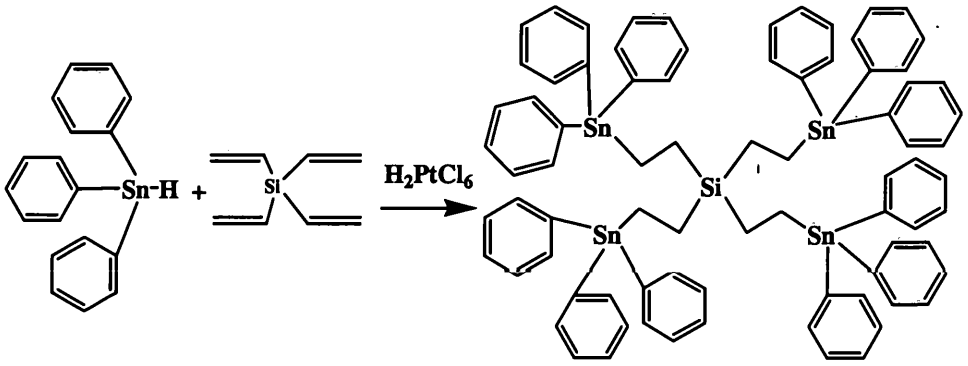
In order to obtain an X-ray crystal structure of a $CyT_6Q_2^V$ we decided to use hydrosilylation to attach a bulky group to the two Q sites on the core. This would not only aid the crystallisation of the cage compound but should prevent disorder, since the bulky groups should crystallise into specific positions.



(3.28)

Scheme 3.27

The radical reaction of tetravinylsilane with triphenyltin hydride had been shown to be one method of attaching bulky triphenyltin groups to a vinylsilane, as shown in Scheme 3.28.



(3.29)

Scheme 3.28

The use of radical reaction would also reduce the amount of cage degradation.

Thus, $CyT_6Q_2^V$ was reacted with triphenyltin hydride using a platinum catalyst. The reaction mixture was stirred at room temperature without any solvent for 24 hours. ^1H NMR showed that most of the vinyl groups remained unreacted. The reaction was repeated using an increased temperature, longer reaction times, a range of solvents and even using a fresh catalyst, however, the ^1H NMR still confirmed that little or no reaction took place. This reaction was repeated using AIBN as an initiator, followed by reflux in toluene, however, the vinyl groups remained in the mixture untouched.

The reaction was repeated using tetravinylsilane as the vinyl substrate and was shown to give the expected product in 68.0% yield compound **3.29**. However, when we used tetramethyldivinyldisiloxane, the reaction with triphenyltin hydride did not occur. This suggests that the triphenyl tin hydride only reacts with vinylsilanes where the silicon is attached to three other carbons. When the silicon is attached to an electron rich oxygen, the reaction does not work. The presence of an O-Si adjacent to the alkene prevents reaction with triphenyl tin possibly because of its electron withdrawing capabilities.

3.3.2.2 Rearrangement of Hexacyclopentylsilsesquioxane in the presence of Q_8^V

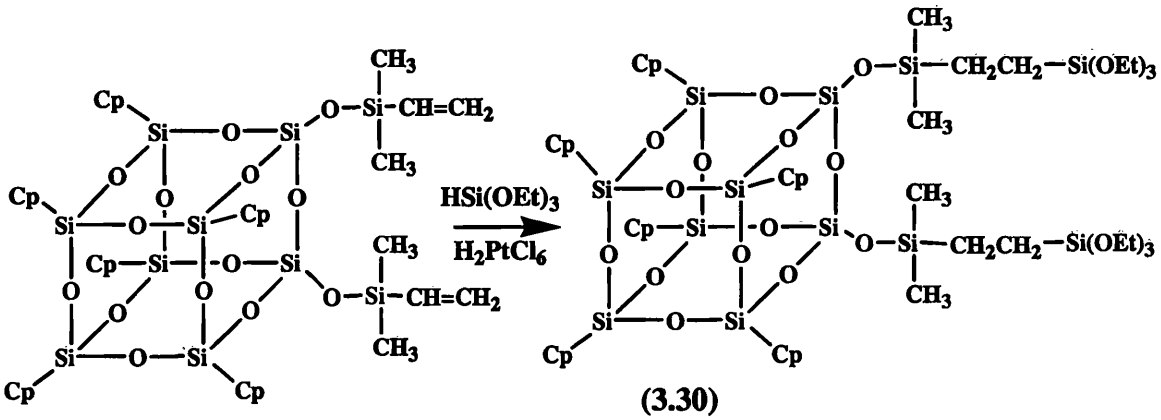
The same reaction conditions were used for the reaction of CpT_6, with TBAF in the presence of Q_8^V. Thus, a 1:2 solution of CpT_6 and Q_8^V in chloroform was stirred overnight

with 0.5 equivalents of TBAF. After removal of the solvent and washing with acetone, a product was obtained in 26.0% yield, which gave ^{29}Si NMR peaks at -0.38, -65.94, -66.50, and -108.37 ppm in a ratio of 1:2:1:1. The spectra again suggest a structure of $CpT_6Q_2^V$ **3.27b**, which was confirmed by MALDI-TOF mass spectrometry.

Hydrosilylated with triethoxysilane in the presence of platinum catalyst was carried out with this $CpT_6Q_2^V$, as shown in3.29.

^{1}H NMR showed the disappearance of the alkene and ^{29}Si NMR showed the formation of the hydrosilylated compound, giving a similar pattern of peaks to compound **3.29** apart from one extra peak for the -Si(OEt)$_3$ group. MALDI-TOF mass spectroscopy confirmed the molecular weight of this cage to be *m/z* 1384 (M+Na$^+$).

The integration in the ^{1}H NMR confirmed that there were two Q arms for every six T arms. However this compound was a wax so that X-ray crystallographic analysis could not be carried out.



(3.30)

Scheme 3.29

3.3.3 Rearrangment of Hexasilsesquioxanes in the presence of Q_8^H

The presence of vinyl groups on the Q silicons of a $T_6Q_2^V$ cage allowed further functionalisation using hydrosilylation. An alternative approach is to have Si-H groups attached to the Q silicons. Thus, a solution of CpT_6 and Q_8^H in chloroform was stirred

overnight with 0.5 equivalents of TBAF. After washing with water, a solid precipitated, which did not dissolve in any common solvents. ^{29}Si NMR analysis of the remaining liquid showed a single peak at -54.36 ppm indicating that the CpT_6 had not reacted. These results suggest that TBAF did not catalyse the rearrangement of the CpT_6 cage but reacted with the Si-H of Q_8^H to give the white solid.

3.4 Rearrangement of Hexasilsesquioxanes in the Presence of Trialkoxysilanes

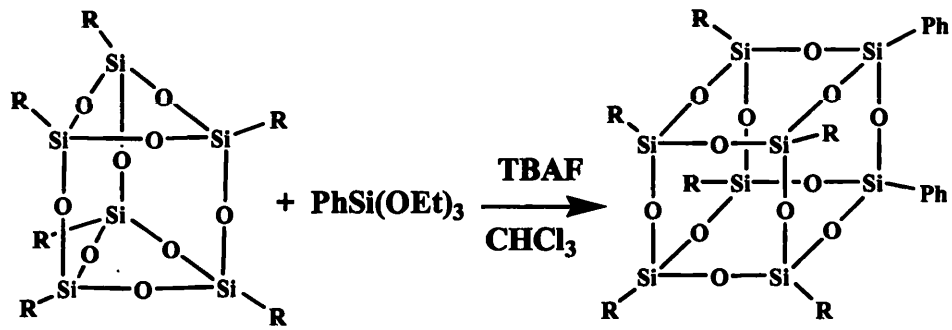
The reaction of hexasilsesquioxanes with TBAF in the presence of spherosilicates, Q_8R_8 suggests that 2 Q units are inserted to form the octahedral cage. Such a controlled synthesis of an octahedral cage structure containing more than one group is clearly very useful and so we developed our methodology to synthesise cage structures of the type $R_6T_6T'_2R'_2$. This involved reaction of the T_6R_6 with TBAF in the presence of alkyltrialkoxysilanes. In general alkyltriethoxysilanes were employed in this reaction, although occasionally an alkytrimethoxysilane was used if it was the only compound available. A variety of alkyltrialkoxysilanes were used, such as phenyltriethoxysilane, allyltriethoxysilane, vinyltrimethoxysilane and methyltriethoxysilane.

3.4.1 Rearrangement of Hexacyclohexylsilsesquioxane in the Presence of Trialkoxysilanes

a) In the presence of Phenyltriethoxysilane

CyT_6 was treated with TBAF in the presence of phenyltriethoxysilane, Scheme 3.30. It was observed that an octahedral cage was formed which had three sharp peaks in the T_8-Si region of the ^{29}Si NMR. The peaks at -68.10 and -68.51 ppm indicated two different environments of silicon atoms linked to an sp^3 carbon of a cyclohexyl group, and single peak at -79.24 suggest a silicon atom connected to an sp^2 carbon of a phenyl group. The integration of these three single peaks is 2:1:1 confirming that there are two phenyl groups

and six cyclohexyl groups on the octahedral core **3.31a**, $CyT_6T'_2{}^{ph}$, and that the phenyl groups are *ortho* to another on the core.

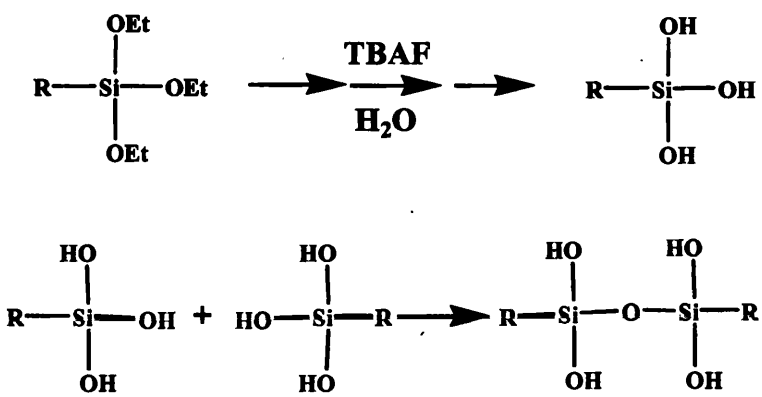


a) R = Cy 26%
b) R = Cp 15%

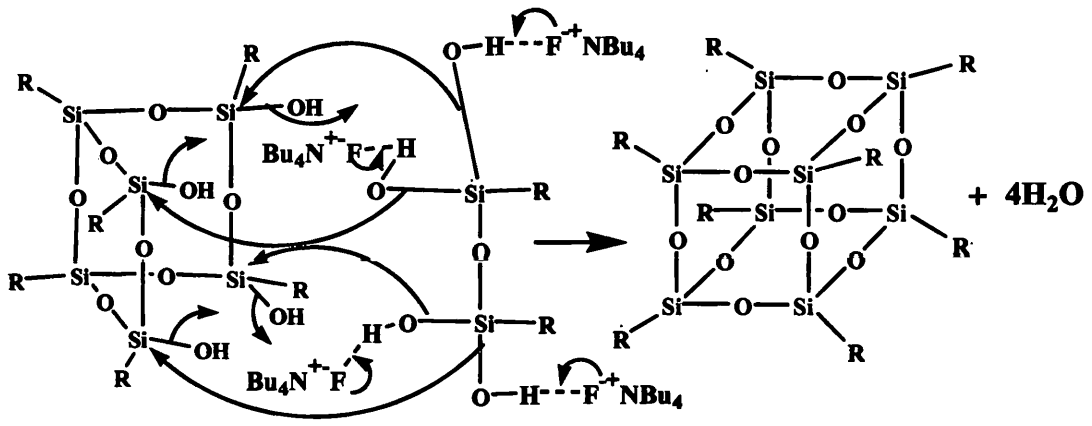
(3.31)

Scheme 3.30

The mechanism of this insertion can be proposed as follow. The previous chapter has demonstrated that alkyltriethoxysilanes can be rearranged to give high molecular weight cages using TBAF, and that open cages with silanol groups were produced as intermediates. Thus, the phenyltriethoxysilane could form a triol species that can condense to give a disiloxane tetrol, Scheme 3.31 and Scheme 3.32.



Scheme 3.31



Scheme 3.32

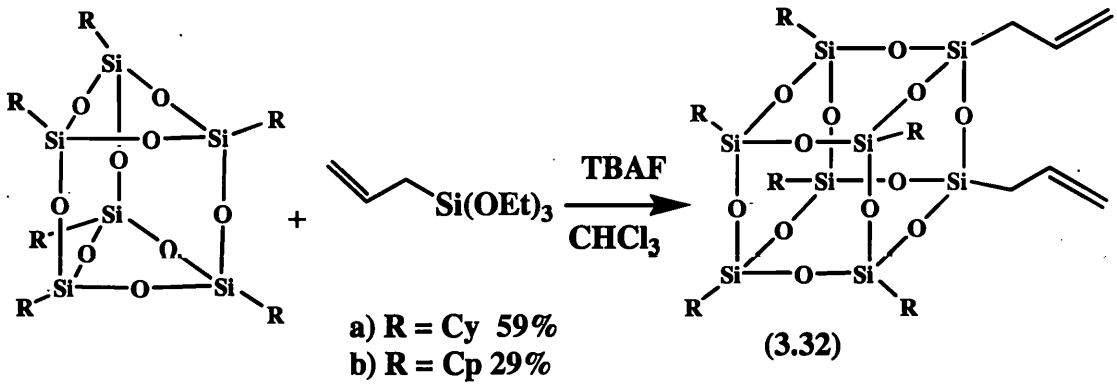
Of course we may also get reaction of one alkyltriethoxysilane group to give a T_7 followed by a second insertion to give T_8.

b) In the Presence of Vinyltrimethoxysilane

To develop the range of funtionalities on the core of the mixed $R_6T_6T_2'R_2'$ cage, vinyltrimethoxysilane was used. As with the phenyltriethoxysilane, this involves a silicon atom attached to an sp^2 carbon, so should be easy to identify using ^{29}Si NMR. However, the vinyl group is much smaller in size than a phenyl group and thus should be easier to insert into an opened cage. Thus the reaction was carried out by stirring a mixture of CyT_6 and TBAF in chloroform in the presence of vinyltriethoxysilane in a ratio 1:10 of CyT_6: vinyltriethoxysilane. The reaction mixture was worked up in the usual way to give a white solid with an oily mixture. After extraction with acetone, a white solid was obtained which ^{29}Si NMR showed mainly contained unreacted CyT_6. An oily residue was obtained after removal of solvent in the acetone fraction. The ^{29}Si NMR showed a major peak at -63 ppm and a couple of small peaks between -55 to -60 ppm. The peak at -63 ppm is suggests a T_6R_6 compound containing a silicon linked to an sp^2 carbon. This could be the result of $vinylT_6$ formation within the reaction. Thus, a reduced amount of vinyltrimethoxysilane should be used in any future rearrangement reactions.

c) In the presence of Allyltriethoxysilane

Allyltriethoxysilane was also used for this insertion reaction, since the C=C bond will provide a potential site for further reaction such as hydrosilylation or bromination. CyT_6 was treated as before with TBAF, but using 1 equivalent of allyltriethoxysilane as shown in Scheme 3.33. The reaction gave a product with two single sharp peaks at -68.64 and -70.99 ppm with a ratio of 3:1. This NMR data indicates that an octahedral CyT_6T_2'allyl was formed, which contained 6 Cy groups and 2 allyl groups. MALDI-TOF data provided confirmation of this type of cage formation. We believed that the 2 allyl groups are *ortho* to each other on the cage, rather than in a *meta* arrangement. This is because if we expand the peak at -68 ppm, we observed a shoulder with ratio of 1:2 in agreement of the type of **3.32a**.



Scheme 3.32

d) In the presence of p-methoxyphenylpropyltriethoxysilane

A chloroform solution of CyT_6 and *p*-methoxyphenylpropyltriethoxysilane in a ratio of 1:2 was stirred at room temperature with 0.5 equivalent of TBAF. After overnight stirring, the reaction mixture was extracted with water. A white solid was obtained after removal of the solvent from the organic layer. ^{29}Si NMR showed a group of peak between -59 and -71 ppm. The pattern and integration of these peaks indicate that the mixture contained CyT_9OH (-59.31, -67.85, -70.10, -70.34, and -70.65 ppm with a ratio of 1:2:2:2:2) and CyT_8 -68.69 ppm. On the other hand, the starting material, *p*-

methoxyphenylpropyltriethoxysilane had disappeared completely, possibly forming the corresponding T_8, as described in the last chapter. This *p*-methoxyphenylpropylT_8 cage did not show up in the ^{29}Si NMR because of its low concentration in the mixture. In other words, the condensation of *p*-methoxyphenylpropyltriethoxysilane may have been faster than the degradation of CyT_6 so that there was no formation of $R_6T_6T'_2R'_2$.

e) In the presence of methyltriethoxysilane

The methyl group is the smallest of all the alkyl groups. If a $T_6T'_2$ cage could be prepared with two methyl groups on the core, their small size, compared to the cyclohexyl group, may prevent disorder in the packing, enabling analysis by X-ray crystallography. Thus CyT_6 was reacted with TBAF in the presence of methyltriethoxysilane and stirred overnight. Extraction with water followed by removal of the solvent from the organic layer gave a white solid. ^{29}Si NMR showed only one single peak at -56.60 ppm, corresponding to the starting material CyT_6. There was no sign of the methyltriethoxysilane starting material. This suggests that, because of the size of the group, the methyltriethoxysilane quickly condensed to give a resin before degradation of the CyT_6 by the TBAF.

3.4.2 Rearrangement of Hexacyclopentylsilsesquioxane in the Presence of Trialkoxysilanes

a) In the presence of Phenyltriethoxysilane

Similar work was carried out with different T_6R_6 cages such as hexacyclopentylsilsesquioxane, CpT_6. The previous reactions of CpT_6 using TBAF suggested that this cage opened more quickly with TBAF than CyT_6.

Phenyltriethoxysilane and cyclopentylhexasilsesquioxane were dissolved in chloroform with TBAF. After stirring overnight, the reaction mixture was extracted with water. After removal of the solvent to give a solid product which showed three peaks in the ^{29}Si NMR at -65.98, -66.33 and -79.37 ppm. These three peaks are all in the T_8-Si region. A silicon

atom linked to an sp^2 carbon would be about 10 ppm upfield of a silicon atom linked to an sp^3 carbon. Thus, the single peak at -79.37 ppm corresponds to a silicon atom attached to a phenyl group and the other two peaks correspond to silicon atoms attached to cyclopentyl groups. The integration of these peaks is 2:1:1, indicating that the arrangement of the two phenyl groups should be *ortho* to each other, as compound **3.31b** and given in15.3% yield.

b) In the presence of allyltriethoxysilane

Reaction of CpT_6 with TBAF was carried out in the presence of allyltriethoxysilane in chloroform. The reaction mixture was then worked up in the usual way to give a white solid. ^{29}Si NMR showed three of peaks between -66.48 ppm and -66.54 ppm, and another three peaks between -71.02 and -71.1 ppm with the same pattern, which occur in the T_8-Si cage region. The NMR suggests compound **32b** was obtained and given in 29.6% yield. Attempts to isolate products by fractional recrystallisation ere not successful, and MALDI-TOF mass spectroscopy did not work for this mixture. Further separation using chromatography would be useful.

c) In the presence of vinyltrimethoxysilane

The reaction of CpT_6 with TBAF in the presence of vinyltriethoxysilane was carried out as before with CyT_6. Thus the reaction was carried out by stirring a mixture of CpT_6 and TBAF in chloroform in the presence of vinyltriethoxysilane in a ratio 1:10 of CpT_6: vinyltriethoxysilane. The reaction gave the same outcomes as that of CyT_6. Thus the ratio of CpT_6 and TBAF need to be optimised in future work.

d) In the presence of methyltriethoxysilane

Although the reaction of CyT_6 with TBAF in the presence of methyltriethoxysilane was not successful, CpT_6 may be a better candidate because of the faster degradation of CpT_6 with TBAF. Thus CpT_6 and methyltriethoxysilane were reacted with TBAF in chloroform. However, ^{29}Si NMR suggests a gel formation rather than well defined cages.

3.4.3 Rearrangement of hexa-*p*-methoxyphenylpropylsilsesquioxane in the Presence of Trialkoxysilanes

a) In the presence of methyltriethoxysilane

Although no reaction occurred with CyT_6 and CpT_6 in the presence of methyltriethoxysilane using TBAF, the rearrangement reaction of *p*-methoxyphenylpropylT_6 occurred much faster. Thus, the rapid cleavage of *p*-methoxyphenylpropylT_6 could quickly provide open cage species that could intercept the $MeSiO_{3/2}$ units before they formed a resin. The reaction of *p*-methoxyphenylpropylT_6 with TBAF was carried out in the presence of methyltriethoxysilane. The reaction mixture was worked up in the usual way. A white solid was obtained from the mixture, which showed a single peak at -66.79 ppm and is identical that from *p*-methoxyphenylpropylT_8. This suggests that *p*-methoxyphenylpropylT_6 degradation is not fast enough to match the condensation of methyltriethoxysilane.

b) In the presence of vinyltrimethoxysilane

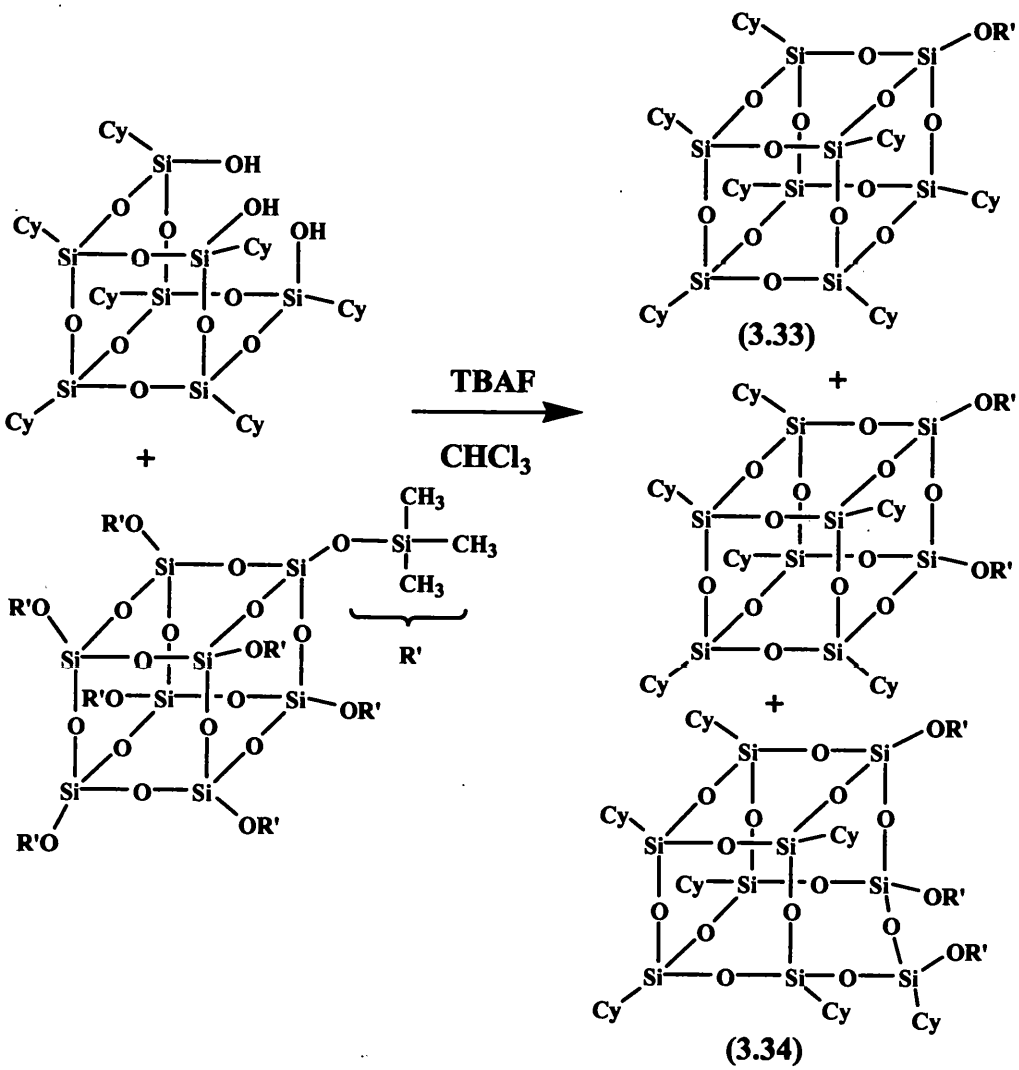
The reaction of *p*-methoxyphenylpropylT_6 with TBAF in the presence of vinyltrimethoxysilane was carried out as before. After overnight stirring the reaction was stopped by extraction with water. A white solid gel was obtained after removal of the solvent from the organic layer. The ^{29}Si NMR showed a number of peaks, which is too complex to identified.

3.5. Rearrangement of partial cages in the presence of Q_8^M

3.5.1 Rearrangement of $CyT_7(OH)_3$ in the presence of Q_8^M

In the last section we showed that $CyT_7(OH)_3$ rearranged to give CyT_9OH and CyT_8. It would be interesting to find out whether a similar insertion of Q units occurs with $CyT_7(OH)_3$. Thus $CyT_7(OH)_3$ was reacted with TBAF in the presence of Q_8^M in

chloroform overnight. The reaction mixture was worked up in the usual way. The white solid obtained in the reaction showed 5 main peaks in the ^{29}Si NMR at 11.40, 11.13, -68.09, -68.64 and -108.26 ppm. Since there are two peaks in the OTMS region, at 11.40, 11.13 ppm, it suggests that there are at least two compounds in the mixture. This mixture was separated by chromatography using hexane to give two main fractions. ^{29}Si NMR and MALDI-TOF mass spectroscopy showed that the first fraction was the CyT_7Q cage with one OTMS on the core **3.33**. The second fraction showed a single peak in the ^{29}Si NMR, but MALDI-TOF mass spectrometry suggest there were two compounds present. One of the cages is probably present in a low concentration which is enhanced in the MALDI-TOF process but which did not register in the NMR. Mass spectroscopic data indicated that these two compounds were $CyT_6Q_2^M$ and $CyT_6Q_3^M$ cages **3.34**. This suggests the overall reaction process shown in reaction Scheme 3.34.



Scheme 3.34

This shows that a Q unit is inserted into a $CyT_7(OH)_3$ cage to form a CyT_7Q^M cage. 3 Q units can also be inserted to give a $CyT_6Q_3{}^M$ cage, which must happen during the rearrangement from $CyT_7(OH)_3$. Presumably the $CyT_7(OH)_3$ partial cage is broken down to a $CyT_6(OH)_4$ ladder which then react with Q units to give other products. The $CyT_6Q_2{}^M$ is probably formed by a similar rearrangement. Again, it highlights the importance of the competition between the rearrangement of $CyT_7(OH)_3$ and the degradation of $Q_8{}^M$.

3.5.2 Rearrangement of $CyT_6(OH)_4$ in the presence of $Q_8{}^M$

$CyT_6(OH)_4$ was reacted with TBAF in the presence of $Q_8{}^M$ in chloroform overnight. The reaction mixture was worked up in the usual way. A white solid from the reaction showed five main peaks at 11.45, 11.13, -68.07, -68.64 and -108.28 ppm. The pattern of peaks

from this reaction mixture was not very different from that obtained from reaction of $CyT_7(OH)_3$. This mixture was separated by chromatography to give two main fractions. ^{29}Si NMR and MALDI-TOF mass spectroscopy showed that the first fraction was the CyT_7Q^M cage compound **3.33** with one OTMS group on the core. The ^{29}Si NMR of the second fraction showed no change in the chemical shift compared to the mixture, but unfortunately, MALDI-TOF mass spectroscopy failed to give any peaks for this second fraction.

3.6 Conclusion for Chapter Three

We have used a range of different approaches for the synthesis of hexasilsesquioxane, T_6R_6 cages. The rearrangement of the hexasilsesquioxane cages was also undertaken. The reaction of hexasilsesquioxane with TBAF gave higher molecular weight cages. The rearrangement reactions were monitored by both of NMR and HPLC. A number of intermediates were observed, such as partial cages, such as $R_6T_6(OH)_4$, $R_7T_7(OH)_3$ and R_9T_9OH. These results suggest that T_6R_6 had undergone cleavages of the Si-O-Si linkages to give partial cages, which subsequently to give higher molecular weight and symmetrical octasilsesquioxane cages.

TBAF is an excellent catalyst for silsesquioxane rearrangement and can be used to rearrange T_6 cages in the presence of spherosilicate cages and alkyltrialkoxysilanes to give $R_6T_6Q_2R'_2$ and $R_6T_6T'_2R'_2$ cages. Although the reaction conditions have to be optimised for some cages, we are convinced that it is an efficient route to obtain heterosubstituted silsesquioxane cages.

3.7 Chapter Three References

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Chapter 4: Experimental

4.0 General Notes

a) NMR spectroscopy

All the NMR spectra were obtained using either a JEOL EX 400 NMR or a JEOL lambda 300 NMR spectrometer. The pulse delay for ^{29}Si spectra was standardised at 20 seconds unless stated otherwise.

Unless stated otherwise all spectra was recorded at room temperature (25°C) using deuterated chloroform ($CDCl_3$) dried over 4 Å molecular sieves as solvent. The NMR external reference compound was TMS for ^{1}H, ^{13}C and ^{29}Si NMR spectra and $CFCl_3$ for ^{19}F NMR spectra. The spectral data point position of these compounds was accurately located before acquisition.

^{29}Si NMR "Stack Experiments" were carried out using a JEOL EX 400 NMR. The NMR spectra were obtained by time. In general, the data were collected each hour for a period of certain hours. However, the timing programme was set up for individual case dependent upon the concentration of the sample and number of scans.

b) Micro-analysis

Microanalysis was performed by MEDAC Ltd. of Brunel University. Where possible, elemental analyses have been reported. Work within the group over a number of years has shown that it is often very difficult to get accurate elemental analysis for some organosilicon compounds, in particular the silsesquioxane cage compounds. Despite repeated submission of samples that have passed every other purity tests. Silicon carbide formation leads to percentages that are consistently less than expected. Thus many of the compounds have one figure which falls short of ideal values and have not been quoted.

c) Mass Spectrometry

Where possible, the mass spectrum has been reported. Work within the group over a number of years has shown that it is often very difficult to get mass spectra for some organosilicon compounds and in particular cages, which did not dissolved in the solvent or matrix used for analysis and thus showed no evidence of the expected.

Lower resolution mass spectra were recorded on a VG 20-250 mass spectrometer or performed by the National Mass Spectrometry Service Centre based at the University of Wales, Swansea. Matrix Assisted Laser Desorption/Ionisation - Time of Flight (MALDI-TOF) has been found to be particularly useful mass spectrometry for cage compounds and analysis have been carried out by University of Southampton. Unless stated otherwise the analysis used (DBH) as a matrix and dichloromethane as a solvent.

d) Melting Point

These were determined on an Electrothermal Digital melting point apparatus and are uncorrected.

e) FT-IR

Infrared spectra were obtained as neat samples or nujol mulls using sodium chloride plates using a Nicolet 205 FT-IR spectrometer or Perkin-Elmer 1710 Infrared Fourier Transform Spectrometer.

f) X-Ray Crystallography

The X-ray crystallographic analysis of compounds was performed by EPSRC X-ray crystallography service at the University of Southampton.

g) Solvents

The following solvents were dried before use:

Diethyl ether - dried over sodium wire.

Chloroform	- dried using magnesium sulphate or 4Å molecular sieves.
Acetone	- dried using magnesium sulphate.
THF	- dried by distillation from sodium wire containing benzophenone and stored under nitrogen before use.

h) Chemicals

All chemical handling, reactions and work-up were performed in an efficient fume cupboard. Reagents were obtained primarily from the Aldrich Chemical Company, Lancaster Ltd. and Gelest Ltd.. Reagents and many silanes were stored under nitrogen, the transference of moisture sensitive liquid reagents was achieved by appropriated syringes fitted with a needle with point tips to minimise damage to septa seals.

Unless state otherwise TBAF was a 1 molar solution in THF containing 5% of water and the platinum catalyst was a 0.02 molar solution of H_2PtCl_6 in *iso*-propyl alcohol.

All new compounds from this work are highlight with "* " at the end of the title.

i) High Performance Liquid Chromatography (HPLC)

High Performance Liquid Chromatography (HPLC) of cages and partial cages used an Alltech Varex MKIII Evaporative Light Scatering Detector (ELSD) and an Alltech 525 HPLC pump. The eluent and column used will be stated for the individual cases.

The detector conditions are:

Drift tube temperature: 80°C	Exhaust temperature: 46°C
Gas pressure: 36.5 psig	Gas flow rate: 2.46 slpm (Standard Litre per Minute)
Solvent pressure: 2.0 psig	Flow rate of eluent: 1ml/min

Attenuation of detector: 1/2

Gel Permeation Chromatography (GPC) was used to analyse some of the product mixtures, coupled to an ELSD. HPLC grade toluene was employed as eluent as required by the

baseline noise for the ELSD. A PL gel 5μl GPC column was used. The conditions used for the detector are:

Drift tube temperature: 80°C	Exhaust temperature: 50°C
Gas flow rate: 2.25 slpm	Gas pressure: 36.5psig
Solvent pressure: 2.2 psig	Flow rate of eluent: 1ml/min
Attenuation of detector: 1/2	

4.1 Synthesis and Rearrangement of Silsesquioxane and Spherosilicate Cages

4.1.1 Synthesis of Alkyltriethtoxysilanes

4.1.1.1 Synthesis of Cyclopentyltriethoxysilane 2.1*

Ethanol (14.46 g, 314.24 mmol) and triethylamine (43.69 g, 314.24 mmol) were dissolved in THF (200 ml) and a solution of cyclopentyltrichlorosilane (20 g, 89.2 mmol) in THF (100 ml) added to the mixture very slowly. After stirring for 1 hour, a white solid precipitated out. The mixture was filtered by vacuum, and the filtrate liquid collected. A yellow liquid was obtained after removal of solvent and was used at the next stage without further purification. (17.70 g, 77.7% yield); ν_{max} (Neat)/cm^{-1} 2983, 2960, 2879, 2768, 2730, 1454, 1387, 1297, 1239, 1172, 1112, 1083, 949 and 778; δ_H (300 MHz; $CDCl_3$) 3.72 (6H, q, OCH_2), 1.53 (2H, m, vbr, CH_2 of Cp), 1.34 (6H, m, vbr, CH_2 of Cp), 1.07 (9H, t, OCH_2CH_3) and 0.87 (1H, m, vbr, CH of Cp); δ_C (75.5 MHz; CDCl3) 58.37 (OCH_2), 27.51 (CH_2), 26.79 (CH_2), 22.85 (CH) and 18.29 (OCH_2CH_3); δ_{Si} (79.3MHz; $CDCl_3$) -46.53.

4.1.1.2 Synthesis of Cyclohexyltriethoxysilane 2.2*

Ethanol (4.66g, 101.3mmol) and triethylamine (10.25 g, 101.3 mmol) were dissolved in THF (200 ml) and a solution of cyclohexyltrichlorosilane (6.89 g, 31.6 mmol) in THF (100 ml) added to the mixture very slowly. After stirring for 1 hour, a white solid precipitated

out. The mixture was filtered by vacuum, and the filtrate liquid collected. A yellow liquid was obtained after removal of solvent, and was used at the next stage without further purification. (6.67g, 85.8% yield); ν_{max} (Neat)/cm^{-1} 2975, 2923, 2875, 2760, 2730, 1484, 1454, 1387, 1357, 1305, 1268, 1201, 1164, 1098 (SiOSi), 1038, 1001, 949, 890, 853, 823, 786, 741 and 675; δ_H (300 MHz; $CDCl_3$) 3.68 (6H, t, CH_2CH_3), 1.68 (5H, m, vbr, CH_2 of Cy), 1.12 (9H, t, J 4.5, CH_2CH_3), 1.09 (5H, m, vbr, CH_2 of Cy) and 0.73 (1H m, vbr, CH of Cy); δ_C (75.5 MHz; $CDCl_3$) 58.37 (OCH_2), 27.51 (CH_2), 26.79 (CH_2), 22.85 (CH) and 18.29 (CH_2CH_3); δ_{Si} (79.3 MHz; $CDCl_3$) -48.86; *m/z* (EI) 247 (M^+), 218, 108, 152, 136, 124 and 80.

4.1.1.3 Synthesis of Benzyltriethoxysilane 2.3*

Ethanol (3.2 g, 70.9 mmol) and triethylamine (7.17 g, 70.9 mmol) were dissolved in THF (100 ml) and a solution of benzyltrichlorosilane (5 g, 22 mmol) in THF (100 ml) added to the mixture very slowly. After stirring for 1 hour, a white solid precipitated out. The mixture was filtered by vacuum, and the filtrate liquid collected. A yellow liquid was obtained after removal of solvent and was used at the next stage without further purification. (4.63 g, 82.8% yield); ν_{max} (Neat)/cm^{-1} 3094, 3064, 3027, 2975, 2931, 2901, 2775, 2730, 1595, 1498, 1454, 1387, 1298, 1261, 1164, 1105, 1075, 1023, 964, 801, 764, 734 and 704; δ_H (300 MHz; $CDCl_3$) 7.16-7.00 (5H, m, CH of Ar), 3.64 (6H, q, CH_2CH_3), 2.12 (2H, s, $SiCH_2$) and 1.10 (9H, t, *J* 11.35, CH_3); δ_C (75.5 MHz; $CDCl_3$) 137.49 (CH of Ar), 128.66 (CH of Ar), 128.10 (CH of Ar), 124.49 (C of Ar), 58.59 (OCH_2), 20.31 ($CH_2C_6H_5$) and 18.34 (CH_3); δ_{Si} (79.3 MHz; $CDCl_3$) -51.22; *m/z* (EI) 255 (M^+), 226, 180, 152, 136, 108 and 91.

4.1.1.4 Synthesis of *p*-Methoxyphenylpropyltriethoxysilane 2.4*

Ethanol (2.59 g, 56.4 mmol) and triethylamine (5.7 g, 56.4 mmol) were dissolved in THF (100 ml), and a solution of 3-*p*-methoxyphenylpropyltrichlorosilane (5 g, 17.6 mmol) in

THF (100 ml) added to the mixture very slowly. After 1 hour stirring, a white solid was precipitated out. The mixture was filtered by vacuum, the filtrate liquid collected. A yellow liquid was obtained after removal of solvent and was used at the next stage without further purification. (4.74 g, 86.0% yield); ν_{max} (Neat)/cm^{-1} 2983, 2931, 2886, 2842, 2768, 2723, 1610, 1573, 1513, 1461, 1432, 1387, 1298, 1253, 1246, 1172, 1112, 1090, 1038, 9499, 801 and 749; δ_H (300 MHz; $CDCl_3$) 7.09 (2H, d, **CH** of Ar), 6.81 (2H, d, **CH** of Ar), 3.82 (1H, s, OCH_3), 3.54 (6H, q, CH_2CH_3), 2.37 (2H, quintet, $CH_2CH_2CH_2Si$), 1.21 (3H, t, CH_2CH_3) and 0.64 (2H, t, CH_2Si); δ_C (75.5 MHz; $CDCl_3$) 157.61 ($COCH_3$), 134.41 (CCH_2), 129.30 (s, CH of Ar), 113.55 (CH of Ar), 58.23 (OCH_2CH_3), 55.12 (CH_3O), 38.20 (CH_2Ar), 24.95 (s, $CH_2CH_2CH_2Si$), 18.21 (CH_2CH_3) and 9.97 (CH_2Si); δ_{Si} (79.3 MHz; $CDCl_3$) -45.42; Found: C, 61.53; H, 9.20. $C_{16}H_{28}SiO_4$ requires C, 61.50; H, 9.20; *m/z* (EI) 313 (M^+), 270, 256, 238, 227, 210, 196, 165, 121, 107, 91 and 77.

4.1.1.5 Synthesis of Hexyltriethoxysilane 2.5*

1-Hexene (2 g, 0.0238 mol) and triethoxysilane (3.91 G, 0.0238 mol) were placed in a small vial, and 100 µl of a 0.02 M solution of H_2PtCl_6 in isopropyl alcohol was added to the mixture.[1, 2] The mixture was heated at 60 °C, and the reaction followed by IR. The reaction was stopped on the disappearance of the Si-H peak at 2256 cm^{-1} in the IR spectra. The product was purified by flash column using hexane and chloroform (1:1) as eluent. (5.6 g, 94.7% yield); ν_{max} (Neat)/cm^{-1} 2975, 2934, 2894, 1446, 1387, 1305, 1172, 1098, 1083, 957, 890 and 786; δ_H (300 MHz, $CDCl_3$) 0.12 (2H, t, J 8.73, $SiCH_2$), 0.36 (8H, m, CH_2), 0.71 (9H, t, J 7.14, OCH_2CH_3), 1.43 (3H, d, J 7.14, CH_2CH_3) and 3.24 (6H, q, J 8.73, OCH_2CH_3); δ_C (75.5 MHz, $CDCl_3$) 10.37 ($SiCH_2$), 14.08 (CH_2CH_3), 18.29 (OCH_2CH_3), 22.75 (CH_2), 28.92 (CH_2), 31.77 (CH_2), 33.16 (CH_2) and 58.27 (OCH_2CH_3); δ_{Si} (79.3 MHz, $CDCl_3$) -44.98.

4.1.1.6 Synthesis of Octyltriethoxysilane 2.6*

1-Octene (5 g, 0.044 mol) and triethoxysilane (7.32 g, 0.044 mol) were placed in a small vial, and 100 μl of a 0.02 M solution of H_2PtCl_6 in isopropyl alcohol added to the mixture.[2] The mixture was heated at 60 °C, the reaction was followed by IR. The reaction was stopped on disappearance of the Si-H peak at 2256 cm^{-1}. The product was purified by flash column using hexane and chloroform (1:1) as eluent. (11.2 g, 91.0% yield); ν_{max} (Neat)/cm^{-1} 2968, 2931, 2864, 1461, 1420, 1291, 1164, 1112, 1083, 957, 875 and 786; δ_H (300 MHz, $CDCl_3$) 0.60 (2H, t, J 7.5, $SiCH_2$), 0.85 (12H, m, CH_2), 1.22 (9H, t, J 6.96, OCH_2CH_3), 1.94 (3H, heptet, J 6.42, CH_2CH_3) and 3.79 (6H, q, J 6.96, OCH_2CH_3); δ_C (75.5 MHz, $CDCl_3$) 10.40($SiCH_2$), 14.06 (CH_3), 18.25 (OCH_2CH_3), 22.71 (CH_2), 29.18 (CH_2), 31.87 (CH_2), 31.78 (CH_2) and 58.32 (OCH_2CH_3); δ_{Si} (79.3 MHz, $CDCl_3$) -45.03.

4.1.1.7 Synthesis of 5-methylcarboxy-3,3-dimethylpentyltriethoxysilane 2.7*

5-methylcarboxy-3,3-dimethyl-1-pentenoate (2 g, 0.14 mol) and triethoxysilane (2.31 g, 0.014 mol) was placed in a small vial, and 100 μl of a 0.02 M solution of H_2PtCl_6 in isopropyl alcohol was added to the mixture.[2] The mixture was heated at 60 °C, and the reaction followed by IR. The reaction was stopped on disappearance if the Si-H peak at 2256 cm^{-1}. The product was purified by flash column using hexane and chloroform (1:1) as eluent. (2.7 g, 90.4% yield); ν_{max} (Neat)/cm^{-1} 2968, 2931, 2894, 2730, 1743, 1476, 1446, 1387, 1350, 1305, 1239, 1164, 1105, 1046, 957, 890, 778 and 660; δ_H (300 MHz, $CDCl_3$) 0.086 (2H, t, J 8.61, $SiCH_2$), 0.44 (6H, s, $C(CH_3)_2$), 0.68 (9H, t, J 6.96, OCH_2CH_3), 0.90 (2H, t, J 8.67 $CH_2CH_2C(CH_3)_2$), 1.66 (2H, s, $CH_2C(CH_3)_2$), 3.10 (3H, s, OCH_3), 3.27 (6H, q, *J* 6.96, OCH_2CH_3); δ_C (75.5 MHz, $CDCl_3$) 4.35 ($SiCH_2$), 18.27 (OCH_2CH_3), 26.54 ($C(CH_3)_2$) 33.91 ($C(CH_3)_2$) 34.90 (CH_2), 45.07 ($COCH_2$), 51.05 (OCH_3), 58.33 (OCH_2CH_3) and 172.80 (CO); δ_{Si} (79.3 MHz, $CDCl_3$) -44.72.

4.1.2 Reaction of Alkyltrialkoxysilanes with TBAF

Cage structures were confirmed by comparison of spectral data with those of samples where possible.

4.1.2.1 Reaction of Cyclopentyltriethoxysilane 2.10

a) Using chloroform as solvent

Cyclopentyltriethoxysilane (3 g, 1.29 mmol) was dissolved in chloroform (20 ml), then TBAF (6.46 ml of 1 M solution in THF with 5% water) was added. The mixture was stirred at room temperature for 48 hours. A white solid precipitated out, which gave a white solid after filtration. (0.21 g, 13.4% yield); m.p.: < 400° (dec.); ν_{max} (Nujol)/cm^{-1} 2726, 1323, 1249, 1110, 949, 914 and 723; δ_H (300 MHz; $CDCl_3$) 1.72 (16H, m, vbr, CH_2) 1.45 (48H, m, vbr, CH_2), 0.88 (8H, m, vbr, CH); δ_C (75.5 MHz; $CDCl_3$) 27.32 (CH_2), 26.99 (CH_2) and 22.27 (CH); δ_{Si} (79.3 MHz; $CDCl_3$) -66.55, CyT_8.[3]

b) Using acetone as solvent

Cyclopentyltriethoxysilane (1.05 g, 4.53 mmol) was dissolved in acetone (20 ml), then TBAF (2.46 ml of 1 M solution in THF with 5% water) was added. The mixture was stirred at room temperature for 24 hours. A white solid precipitated out, which gave a white solid after filtration. (0.5 g, 94.8% yield); δ_H (300 MHz; $CDCl_3$) 1.70 (16H, m, vbr, CH_2) 1.44 (48H, m, vbr, CH_2), 0.88 (8H, m, vbr, CH); δ_C (75.5 MHz; $CDCl_3$) 27.28 (CH_2), 26.99 (CH_2) and 22.25 (CH); δ_{Si} (79.3 MHz; $CDCl_3$) -66.55.

c) Using THF as solvent

Cyclopentyltriethoxysilane (1.15 g, 4.95 mmol) was dissolved in THF (50 ml), then TBAF (9.91 ml of 1 M solution in THF with 5% water) was added. The mixture was stirred at room temperature for 24 hours. A white solid precipitated out, which gave a white solid after filtration. (0.14 g, 23.4% yield); δ_H (300 MHz; $CDCl_3$) 1.65 (16H, m, vbr, CH_2) 1.41

(48H, m, vbr, CH_2), 0.85 (8H, m, vbr, CH); δ_C (75.5 MHz; $CDCl_3$) 27.25 (CH_2), 26.97 (CH_2) and 22.23 (CH); δ_{Si} (79.3 MHz; $CDCl_3$) -66.55.

4.1.2.2 Reaction of Cyclohexyltriethoxysilane 2.11

Cyclohexyltriethoxysilane (1.22 g, 4.95 mmol) was dissolved in acetone (20 ml), then TBAF (2.47 ml of 1 M solution in THF with 5% water) was added. This mixture was stirred at room temperature for 24 hours. A white solid precipitated out, and a white solid was obtained after filtration. (0.5 g, 83.6% yield); m.p.: < 400° (dec.); ν_{max} (Nujol)/cm^{-1} 2667, 1348, 1269, 1197, 1111, 1039, 1027, 999, 895, 849, 827 and 724; δ_H (300 MHz; $CDCl_3$) 1.19 (40H, vbr, m, CH_2), 0.72 (40H, vbr, m, CH_2) and 0.21 (8H, vbr, m, CH); δ_C (75.5 MHz; $CDCl_3$) 27.61 (CH_2), 26.74 (CH_2) and 23.27 (CH); δ_{Si} (79.3 MHz; CDCl3) -68.69.[4, 5]

4.1.2.3 Reaction of *iso*-Butyltrimethoxysilane 2.12*

Iso-Butyltrimethoxysilane (3.11g, 17.4mmol) was dissolved in $CHCl_3$ (100 ml), then TBAF (8.72 ml of 1 M solution in THF with 5% water) was added. This mixture was stirred at room temperature for 48 hours, then washed with water (3 × 200ml). A white solid with an oily gel was obtained after removal of the solvent. The residue was washed with a mixed solvent of chloroform and acetone (1:5) to give a white solid after filtration (0.2 g, 14.7% yield); m.p.: 268°C; ν_{max} (Nujol)/cm^{-1} 2732, 2627, 1417, 1328, 1231, 1120, 1046, 964, 845, 756 and 697; δ_H (300 MHz; $CDCl_3$) 1.85 (8H, nonlet, CH), 0.93 (48H, d, CH_3) and 0.54 (16H, d, $SiCH_2$); δ_C (75.5 MHz; $CDCl_3$) 25.65 (CH_3), 23.82 (CH) and 22.48 (CH_2Si); δ_{Si} (79.3 MHz; $CDCl_3$) -67.90.

4.1.2.4 Reaction of Octyltriethoxysilane 2.13, 2.14

Octyltriethoxysilane (3.09 g, 11.2 mmol) was dissolved in $CHCl_3$ (100 ml), then TBAF (5.58 ml of 1 M solution in THF with 5% water) was added. This mixture was stirred at

room temperature for 48 hours, then washed with water (3 × 200 ml). A colourless wax was obtained after removal of the solvent. (1.2g in total, yield 56% of T_8 and 26% of T_{10} calculated by NMR); ν_{max} (Nujol)/cm^{-1} 2723, 2671, 1409, 1298, 1268, 1231, 1261, 1120, 882, 793, 771, 741, 726 and 689; δ_H (300 MHz; $CDCl_3$) 1.25 (vbr, m, CH_2), 0.85 (*t*, CH_3) and 0.61 (*t*, $SiCH_2$); δ_C (75.5 MHz; $CDCl_3$) 32.89, 32.69, 31.96, 29.37, 29.32, 29.27 (CH_2), 22.98, 22.79, 22.71 (CH_3), 14.11, 13.58 and 11.97 ($SiCH_2$); δ_{Si} (79.3 MHz; $CDCl_3$) -66.64 (**Si** of T_8) and -68.57 (**Si** of T_{10}).[6-8]

4.1.2.5 Reaction of Hexyltriethoxysilane 2.15, 2.16

Hexyltriethoxysilane (3.37 g, 13.5 mmol) was dissolved in $CHCl_3$ (100 ml), then TBAF (6.78 ml of 1 M solution in THF with 5% water) was added. This mixture was stirred at room temperature for 48 hours, then washed with water (3 × 200 ml). After removal of the solvent, a colourless waxy product was obtained. (0.14 g in total, 50% of T_8 and 21% of T_{10} yield calculated by NMR); ν_{max} (Nujol)/cm^{-1} 2732, 2649, 1417, 1343, 1298, 1253, 1224, 1194, 1112, 1038, 957, 890, 808, 764 and 694; δ_H (300 MHz; $CDCl_3$) 1.27 (vbr, m, CH_2), 0.98 (vbr, m, CH_3) and 0.68 (vbr, m, $SiCH_2$); δ_C (75.5 MHz; $CDCl_3$) 32.53, 32.33, 31.60, 31.57 (CH_2), 22.93, 22.74, 22.57, 22.56 (CH_2) 14.10, 12.62 and 11.98 ($SiCH_2$); δ_C (79.3 MHz; $CDCl_3$) -66.68 (**Si** of T_8) and -68.62 (**Si** of T_{10}); *m/z* (MALDI-TOF, DHB matrix) 1373.83 (100%, M of T_{10} + Na^+) and 1097.70 (71%, M of T_8 + Na^+)

4.1.2.6 Reaction of Methyltriethoxysilane[9]

The reaction of methyltriethoxysilane with TBAF was carried out in the same way as other alkyltriethoxysilanes. Unfortunately, the reaction failed to give any identifiable product.

4.1.2.7 Reaction of Allyltriethoxysilane 2.17, 2.18, 2.19

Allyltriethoxysilane (2.3 g, 11.3 mmol) was dissolved in $CHCl_3$ (100 ml), then TBAF (5.62 ml of 1 M solution in THF with 5% water) was added. This mixture was stirred at room temperature for 24 hours. The mixture was dried using 4 Å molecule sieve, then TMSCl (6.2 g, 57 mmol) was added, and the mixture stirred overnight. The molecular sieve was removed by filtration, and the filtrate collected. A yellow gel mixture of products was obtained after removal of solvent. (0.5 g in total, 3% of T_8, 76% of T_{10} and 21% of T_{12} yield calculated by NMR); ν_{max} (Neat)/cm^{-1} 2723, 2684, 1693, 1491, 1135 (SiOSi), 994, 942, 890, 764 and 637; δ_H (300 MHz; $CDCl_3$) 5.13-5.05 (m, **CH**), 4.53-4.25 (m, $\mathbf{CH_2}$) and 1.19-0.82 (m, $\mathbf{SiCH_2}$); δ_C (75.5 MHz; $CDCl_3$) 13.17 ($\mathbf{SiCH_2}$), 114.53-114.36 (**CH**), 131.66-131.07 ($\mathbf{CHCH_2}$); ^{29}Si NMR (79.3 MHz; $CDCl_3$) -71.49 (**Si** of T_8), -73.37 (**Si** of T_{12}), -73.61 (**Si** of T_{10}), -76.05 (**Si** of T_{12}), 187.23 (sept, *J* 225Hz, SiF).

4.1.2.8 Reaction of Vinyltrimethoxysilane 2.20, 2.21, 2.22

Vinyltrimethoxysilane (2.1 g, 14 mmol) was dissolved in $CHCl_3$ (100 ml), then TBAF (7.08 ml of 1 M solution in THF with 5% water) was added. This mixture was stirred at room temperature for 24 hours. The mixture was dried using 4 Å molecule sieve, then TMSCl (12.45 g, 668 mmol) was added, and the mixture stirred overnight. The molecular sieve was removed by filtration, and the filtrate collected. A yellow solid gel was obtained after removal of the solvent. A yellow crystalline solid product was obtained using fractional recrystallisation from a mixed solvent of hexane/chloroform (7:3). (0.45g in total, 1% of T_8, 45% of T_{10} and 54% T_{12} yield calculated by NMR); ν_{max} (Nujol)/cm^{-1} 2723, 2678, 1654, 1595, 1283, 1253, 1127 (SiOSi), 1016, 964, 897, 838 and 756; δ_H (300 MHz; $CDCl_3$) 6.03-5.72 (m, $\mathbf{CH{=}CH_2}$); δ_C (75.5 MHz; $CDCl_3$) 130.1-128.6 (**CH**), 136.9-136.1 ($\mathbf{CH_2}$); δ_{Si} (79.3 MHz; $CDCl_3$) -80.19 (**Si** of T_8), -81.48 (**Si** of T_{10}) and -81.33, -83.34

(1:2) (Si of T_{12}); *m/z* (MALDI-TOF, DHB matrix) 814.52 (54%, M of T_{10} + Na), 972.39 (86%, M of T_{12} + Na), 187.42 (sept, *J* 224Hz, SiF)..

4.1.2.9 Reaction of Phenyltriethoxysilane 2.23

Phenyltriethoxysilane (2.56 g, 10.6 mmol) was dissolved in $CHCl_3$ (150 ml), then TBAF (5.32 ml of 1 M solution in THF with 5% water) was added. This mixture was stirred at room temperature for 3 days. After filtration and drying in an oven, a white solid product was obtain (1.0 g, 48.7% yield); m.p.: <400 (dec.); ν_{max} (Nujol)/cm^{-1} 3072, 3057, 1602, 1432, 1120, 946, 741 and 697; δ_{Si} (79.3 MHz; CPMAS) -76.82 and -80.40; *m/z* (MALDI-TOF, DHB matrix) 1573.02 (100%, $[M + Na^+]$) and 1658.85 (95%, $[M + Ag^+]$).

4.1.2.10 Reaction of Benzyltriethoxysilane 2.24, 2.25, 2.26

Benzyltriethoxysilane (1.34 g, 5.27 mmol) was dissolved in $CHCl_3$ (50 ml), then TBAF (2.63 ml of 1 M solution in THF with 5% water) was added. This mixture was stirred at room temperature overnight. The mixture was washed with water (3 × 50 ml). The organic layer was separated, and a yellow oil was obtained after removal of the solvent. (0.36 g in total, 2% of T_8, 88% of T_{10} and 10% of T_{12} Yield calculated by NMR) ν_{max} (Neat)/cm^{-1} 3087, 3057, 3020, 2923, 2886, 1602, 1491, 1454, 1402, 1209, 1194, 1187, 1105, 1031, 905 and 823; δ_H (300 MHz; $CDCl_3$) 1.69 (20H, s, CH_2), 6.72 (CH_2 of Ar) and 7.02 (CH_2 of Ar); δ_C (75.5 MHz; $CDCl_3$) 21.17 (CH_2), 124.73 (C of Ar), 128.22 (CH_2 of Ar), 128.73 (CH_2 of Ar) and 136.58 (CH_2 of Ar); δ_{Si} (79.3 MHz; $CDCl_3$) T_8: -70.12, T_{10}: -72.68 and T_{12} -70.89, -75.07.[4]

4.1.2.11 Reaction of *p*-Methoxyphenylpropyltriethoxysilane 2.27*

3-*p*-Methoxyphenylpropyltriethoxysilane (1.11 g, 3.54 mmol) was dissolved in $CHCl_3$ (50 ml), then TBAF (1.77 ml of 1 M solution in THF with 5% water) was added. The mixture was stirred at room temperature overnight. The mixture was washed with water (3 × 50

ml). The organic layer was separated. A white solid with an yellow oil was obtained after removal of the solvent. This residue was extracted with acetone (5 ml) to give a white solid after filtration. (0.13 g, 17.1% yield); m.p.:144°C; ν_{max} (Nujol)/cm^{-1} 2730, 2671, 1610, 1580, 1513, 1305, 1253, 1194, 1150, 1023, 823, 771, 734 and 689; δ_H (300 MHz; $CDCl_3$) 6.93 (16H, d, **CH** of Ar), 6.71 (16H, d, **CH** of Ar), 3.69 (24H, s, $\mathbf{CH_3}$), 2.47 (16H, t, $\mathbf{CH_2}$-Ar), 1.78 (16H, pent, $\mathbf{CH_2CH_2}$Ar) and 0.55 (16H, t, Si$\mathbf{CH_2}$); δ_C (75.5 MHz; $CDCl_3$) 158.70 (**C** of Ar), 134.50 (**C** of Ar), 129.36 (**CH** of Ar), 113.76 (**CH** of Ar), 55.28 ($\mathbf{CH_3}$), 37.97 ($\mathbf{CH_2}$Ar), 25.07 ($\mathbf{CH_2CH_2}$Si) and 12.30 (Si$\mathbf{CH_2}$); δ_{Si} (79.3 MHz; $CDCl_3$) -66.77; *m/z* (MALDI-TOF, DHB matrix) 1610.55 (100%, M). Full details of X-ray crystallographic data are shown in Appendix part 3.

4.1.2.12 Reaction of Methyl-3,3-dimethyl-5-triethoxysilylpentanoate 2.28, 2.29*

Methyl-3,3-dimethyl-5-triethoxysilylpentanoate[10] (1.34g, 4.37mmol) was dissolved in $CHCl_3$ (40 ml), then TBAF (2.18 ml of 1 M solution in THF with 5% water) was added. The mixture stirred at room temperature overnight. The mixture was washed with water (3 × 50 ml). The organic layer was separated, and a pale yellow oily solid was obtained after removal of the solvent. (0.8 g in total, 20% of T_8 and 32% of T_{10} yield calculated by NMR. ν_{max} (Neat)/cm^{-1} 2968, 2871, 2263, 1782, 1461, 1439, 1343, 1305, 1246, 1105, 912, 801, 741 and 697; δ_H (300 MHz; $CDCl_3$) 0.51 (*t*, Si$\mathbf{CH_2}$), 0.44 (*s*, $\mathbf{CH_3}$), 0.88 (*t*, $\mathrm{SiCH_2}\mathbf{CH_2}$), 1.72 (*s*, $\mathrm{OCC}\mathbf{H_2}$) and 3.10 (*s*, $\mathrm{OC}\mathbf{H_3}$); δ_C (75.5 MHz; $CDCl_3$) 6.04 ($\mathbf{CH_3}$), 6.61($\mathbf{CH_3}$), 26.46 ($\mathrm{C}(\mathbf{CH_3})_2$), 33.79 ($\mathbf{CH_2}$), 35.29 ($\mathbf{CH_2}$), 44.93 ($\mathbf{CH_2}$), 51.03 ($\mathrm{O}\mathbf{CH_3}$) and 172.64 (**CO**). δ_{Si} (79.3 MHz; $CDCl_3$) T_8: -66.06, T_{10}: -67.97

4.1.2.13. Reaction of 3-Aminopropyltriethoxysilane[10]

The reaction of 3-aminopropyltriethoxysilane with TBAF was carried out in the same way as the other alkytriethoxysilanes, however, the reaction did not give any identifiable products.

4.1.2.14 Reaction of Mercaptopropyltriethoxysilane

The reaction of mercaptopropyltriethoxysilane with TBAF was carried out in the same way as other alkytriethoxysilanes, however, the reaction did not give any identifiable products.

4.1.3 Synthesis of Octasilsesquioxanes

4.1.3 1 Synthesis of 5-Phenoxy-1-pentene 2.30*

5-Bromo-1-pentene (25 g, 167 mmol) and phenol (6.78 g, 72 mmol) were refluxed in dry acetone with potassium carbonate (49.75g) for 3 days. The mixture was filtered, and the solvent distilled from the filtrate. The resulting liquid was distilled under vacuum to give a liquid product. (7.86 g, 31.4% yield); ν_{max} (Neat)/cm^{-1} 3391, 3079, 3042, 2946, 2864, 2857, 1602, 1469, 1394, 1305, 1239, 1172, 1142, 1083, 1031, 994, 912 882, 816, 689 and 667; δ_H (300 MHz, $CDCl_3$) 1.8-2.0 (2H, m, CH_2= CH-C**H**$_2$), 2.1-2.4 (2H, m, CH_2=CH-CH_2-C**H**$_2$), 3.8-4.1 (2H, t, C**H**$_2$-O), 4.9-5.2 (2H, m, C**H**$_2$=CH), 5.8- 6.0 (2H, m, CH_2=C**H**), 6.8-7.0 (3H, m, Ar-**H**), 7.2-7.4 (2H, m, Ar-**H**); δ_C (75.5 MHz, $CDCl_3$) 28.44, (CH_2=CH-**C**H$_2$), 30.12 (**C**H$_2$-CH_2-O), 66.97 (CH_2-**C**H$_2$-O), 114.47 (Ar-**C**), 115.14 (C**H**$_2$=C**H**), 120.52 (Ar-**C**), 129.32 (Ar-**C**), 137.82 (**C**H$_2$=CH), 159.02 (Ar-**C**).

4.1.3.2 Synthesis of Octahydrosilsesquioxane 2.31, $(SiO_{3/2})_8H_8$

Anhydrous $FeCl_3$ (100 g, 616 mmol) and a concentrated HCl (40 ml) were added to a 2 L round bottom flask, followed by methanol (80 ml), hexane (700 ml) and toluene (100 ml). The mixture was stirred using a magnetic stirrer for half an hour. A solution of trichlorosilane (44 ml, 435 mmol) in hexane (300 ml) was added dropwise using a pressure equalising funnel, over a period of six and a half hours. The reaction mixture was stirred for a further half an hour. The upper hexane layer was transferred to another 2 L round bottom flask. Sodium carbonate (28 g, 264 mmol) and calcium chloride (20 g, 180 mmol) were added to the mixture and stirring continued overnight. After filtration, the solvent was

removed using a rotary evaporator. A fine white solid was produced. This solid was recrystallized from hexane to give the pure product as a white needle shaped crystalline solid.[1,11] (1.67 g, 7.3% yield); m.p.:< 300° (dec.); ν_{max} (Nujol)/cm^{-1} 2294 (SiH), 1122, 862, 723; δ_H (300 MHz; $CDCl_3$) 4.24 (8H, s, SiH); δ_{Si} (79.3 MHz; $CDCl_3$) -84.67; *m/z* (FAB): 423(M^+).

4.1.3.4 Synthesis of Octaheptylsilsesquioxane 2.32, $(SiO_{3/2})_8[(CH_2)_6CH_3]_8$

T_8H_8 (0.4 g, 0.94 mmol) and 1-heptene (0.74 g, 7.54 mmol) were added into a small vial, and 10 µl of a 0.02 M solution of H_2PtCl_6 in *iso*-propyl alcohol was added. The mixture was stirred and heated at 80°C. The reaction was followed by IR spectroscopy and reaction was stopped on disappearance of the Si-H peak at 2256 cm^{-1}. The product was purified using a silica gel column using toluene as eluent. A waxy product was obtained after removal of the solvent.[1] (0.90 g, 78.5% yield); m.p 25-27 °C; ν_{max} (Nujol)/cm^{-1} 2730, 2678, 1231, 1179, 1120, 1023, 964, 786, 762, 689 and 660; δ_H (300 MHz; $CDCl_3$) 1.28 (80H, vbr, m, CH_2), 0.95 (24H, s, CH_3) and 0.63 (16H, q, $SiCH_2$); δ_C 34.69, 31.82, 29.05, 22.72 (CH_2), 14.01 (CH_3) and 11.98 ($SiCH_2$); δ_{Si} (79.3 MHz, $CDCl_3$) -66.63.

4.1.3.5 Synthesis of Octaoctylsilsesquioxane2.33, $(SiO_{3/2})_8[CH_3(CH_2)_7]_8$

T_8H_8 (0.6 g, 1.4 mmol) and 1-octene (1.27 g, 11.3 mmol) were added to a small vial, and 10 µl of a 0.02 M solution of H_2PtCl_6 in *iso*-propyl alcohol was added was added. The mixture was stirred and heated at 80°C. The reaction was followed by IR spectroscopy, and reaction was stopped on disappearance of the Si-H peak at 2256 cm^{-1}. The product was purified by chromatography using a silica gel column with toluene as eluent. A waxy product was obtained after removal of the solvent.[1,12] (1.65 g, 89.8% yield); m.p.: 51°C; ν_{max} (Nujol)/cm^{-1} 2750, 2691, 1280, 1232, 1197, 1120, 798, 786 and 709; δ_H (300 MHz; $CDCl_3$) 1.26 (96H, vbr, m, CH_2), 0.93 (24H, t, CH_3) and 0.62 (16H, t, $SiCH_2$); δ_C 32.81

(CH_2), 32.09(CH_2), 29.46(CH_2CH_3), 22.92 (CH_2CH_2Si), 14.23 (CH_3) and 12.08 ($SiCH_2$); δ_{Si} (79.3 MHz; $CDCl_3$) -66.63; *m/z* (EI) 1207 (41.6%, $M^+ - C_8H_{17}$), 1095 and 111.

4.1.3.6 Synthesis of Octanonylsilsesquioxane 2.34, $(SiO_{3/2})_8[CH_3(CH_2)_8]_8$

T_8H_8 (0.40 g, 0.94 mmol) and 1-nonene (0.95 g, 7.54 mmol) were added to a small vial, and 10 μl of a 0.02 M solution of H_2PtCl_6 in *iso*-propyl alcohol was added was added. The reaction mixture was stirred and heated at 80°C. The reaction was followed by IR spectroscopy and the reaction was stopped on the disappearance of the Si-H peak at 2250 cm^{-1}. The product was purified by chromatography using a silica gel column with toluene as eluent. A waxy product was obtained after removal of the solvent.[12] (0.98 g, 72% yield); m.p.: 42-43°C; ν_{max} (Nujol)/cm^{-1} 2731, 2672, 2854, 1408, 1305, 1285, 1264, 1250, 1226, 1207, 1183, 1116, 891, 795, 764 and 722; δ_H (300 MHz, $CDCl_3$) 0.08 (16H, t, *J* 8.43, $SiCH_2$), 0.36 (24H, t, *J* 6.96, CH_3), 0.74 (112H, m, vbr, CH_2); δ_C (75.5 MHz, $CDCl_3$) 11.96 ($SiCH_2$), 14.11 (CH_3), 22.71 (CH_2), 29.38 (CH_2), 29.58 (CH_2), 31.96 (CH_2) and 32.69 (CH_2); δ_{Si} (79.3 MHz; $CDCl_3$) -66.63.

4.1.3.7 Synthesis of Octadecylsilsesquioxane 2.35, $(SiO_{3/2})_8[CH_3(CH_2)_9]_8$

T_8H_8 (0.40g, 0.94mmol) and 1-decene (1.06g, 7.54mmol) were added into a small vial, and 10 μl of a 0.02 M solution of H_2PtCl_6 in *iso*-propyl alcohol was added was added. The reaction mixture was stirred and heated at 80°C. The reaction was followed by IR spectroscopy and stopped on disappearance of the Si-H peak at 2250 cm^{-1}. The product was purified by chromatography using a silica gel column using toluene as eluent. A waxy product was obtained after removal of the solvent.[12] (1.26 g, 86.4% yield); m.p: 54-56°C; ν_{max} (Nujol)/cm^{-1} 2731, 2668, 1408, 1309, 1294, 1272, 1255, 1241, 1219, 1202, 1182, 1113, 888, 850, 774, 722, 708 and 684; δ_H (300 MHz; $CDCl_3$) 1.25 (128H, vbr, m, CH_2),

0.87 (24H, t, CH_3) and 0.59 (16H, t, $SiCH_2$); δ_C (75.5 MHz; $CDCl_3$) 32.67, 31.95, 29.62, 29.37, 22.78 (CH_2), 14.08 (CH_3) and 11.93 ($SiCH_2$); δ_{Si} (79.3 MHz; $CDCl_3$) -66.63.

4.1.3.8 Synthesis of Octadodecylsilsesquioxane2.36, $(SiO_{3/2})_8[CH_3(CH_2)_{11}]$

T_8H_8 (0.41 g, 0.94 mmol) and 1-dodecene (1.30 g, 7.54 mmol) were added into a small vial, and 10 μl of a 0.02 M solution of H_2PtCl_6 in *iso*-propyl alcohol was added was added. The reaction mixture was stirred and heated at 80°C. The reaction was followed by IR spectroscopy and the reaction was stopped on disappearance of the Si-H peak at 2250 cm^{-1}. The product was purified by chromatography using a silica gel column with toluene as eluent. A waxy product was obtained after removal of the solvent.[1,12] (1.4 g, 83% yield); m.p.: 65°C; ν_{max} (Nujol)/cm^{-1} 2731, 2667, 1408, 1310, 1297, 1278, 1270, 1254, 1241, 1226, 1211, 1180, 1116, 942, 923, 891, 869, 802, 776, 761, 722 and 708; δ_H (300 MHz; $CDCl_3$) 1.11 (16H, vbr, m, CH_2), 0.73 (24H, t, CH_3) and 0.45 (16H, t, $SiCH_2$); δ_C 32.78, 32.04, 29.74, 29.50, 22.88 (CH_2), 14.19 (CH_3) and 12.08 ($SiCH_2$); δ_{Si} (79.3 MHz; $CDCl_3$) -66.63.

4.1.3.9 Synthesis of 5-phenoxypentylsilsesquioxane 3.7, $(SiO_{3/2})_8[(CH_2)_5OPh]_8$*

T_8H_8 (0.2g) and 5-phenoxy-1-pentene (0.61g) were added into a small vial, 10 μl of a 0.02 M solution of H_2PtCl_6 in *iso*-propyl alcohol was added. The mixture was stirred and heated at 80°C. The disappearance of the Si-H band ($\lambda \approx 2250$ cm^{-1}) was confirmed by IR spectroscopy. The product was purified by flash column chromatography using 100% toluene as the eluent. The solvent was evaporated to give an oily product. (0.79g, 97.4% yield); ν_{max} (Neat)/cm^{-1} 3057, 3035, 2923, 2857, 1469, 1387, 1335, 1298, 1239, 1098, 971, 875, 793, 764 and 682; δ_H (300 MHz, $CDCl_3$) 0.42 (2H, t, $SiCH_2$), 1.15 (4H, m, $SiCH_2CH_2CH_2$), 1.45 (2H, t, CH_2CH_2O), 3.67 (2H, t, CH_2O), 6.55-6.78 (2H, q, **H** of Ar), 6.90-7.06 (3H, t, **H** of Ar); δ_C (75.5 MHz, $CDCl_3$) 11.73 ($SiCH_2$), 22.45 ($SiCH_2CH_2CH_2$),

28.96 (CH_2CH_2O), 67.67 (CH_2O), 114.41 (C of Ar), 120.43 (C of Ar), 129.02 (C of Ar), 159.07 (C of Ar); δ_{Si} (79.3 MHz, $CDCl_3$) 66.74.

4.1.4 Rearrangement of Octasilsesquioxane Cages

4.1.4.1 Treatment of Octasilsesquioxane with electrophiles

4.1.4.2 Reaction of Octaoctylsilsesquioxane with HBF_4/BF_3[13]

a) "Stack Experiments"

Octaoctylsilsesquioxane (0.0378 g, 0.28 mmol) was dissolved in $CDCl_3$ (2 ml) in a 5 nm NMR tube, and then $HBF_4.OMe_2$ (263 µl) and $BF_3.OEt$ (346 µl) were added. The mixture was mixed for a couple minutes then a "Stack Experiment" was carried out The ^{29}Si NMR spectrum was collected each hour (165 scans) for a period of 16 hours.

b) At a high temperature

Octaoctylsilsesquioxane (0.622 g, 0.47 mmol) was dissolved in $CDCl_3$ (2 ml) in a small vial and $HBF_4.OMe_2$ (263 µl) and $BF_3.OEt$ (346 µl) were added. The mixture was refluxed for 2.5 hours. This mixture was allowed to stand at room temperature overnight, then washed with a saturated solution of sodium bicarbonate. The organic layer was separated and dried with magnesium sulphate. After removal of the solvent, a yellow oily product was obtained. (0.02 g, 68% yield calculated by NMR); ν_{max} (Nujol)/cm^{-1} 2769, 2692, 1317, 1267, 1245, 1225, 1190, 1120, 962, 885, 817, 736, 725, and 690; δ_H (300 MHz, $CDCl_3$) 1.27 (vbr, m, CH_2), 0.85 (m, CH_3) and 0.62 (m, CH_2Si); δ_C (75.5 MHz, $CDCl_3$) 32.93 (CH_2), 32.78 (CH_2), 31.99 (CH_2), 31.64 (CH_2), 29.30 (CH_2), 22.74 (CH_2), 22.71 (CH_2), 22.38 (CH_2), 14.08 (CH_3), 12.30 (CH_3), 11.73 (CH_2Si) and 10.93 (CH_2Si); δ_{Si} (79.3 MHz, $CDCl_3$) -66.63 (Si from starting material, $OctylT_8$), -60.96 (SiF, d, *J* 264), -65.09 ($C_8H_{17}SiO$) and -66.00 (SiOSiF), (1:1:2); δ_F (376 MHz, $CDCl_3$) -138.

c) With excess of amount of HBF_3 and BF_4

OctylT$_8$ (0.3g, 0.028 mmol) was dissolved in $CHCl_3$ (10 ml), then $HBF_4.OMe_2$ (254 μl, 2.09 mmol) and $BF_3.OEt_2$ (334 μl, 2.72 mmol) was added. The mixture was refluxed for 1 hour and allowed the mixture cooled down and stayed at room temperature for overnight. Two phases were observed, the upper layer with some wax suspended was separated from the bottom brown layer. The NMR showed the brown layer was TBAF only. The wax from the upper layer was then analysed by NMR. δ_H (300 MHz, $CDCl_3$) 1.25 (vbr, m, CH_2), 0.89 (t, CH_3) and 0.63 (q, $SiCH_2$); δ_C (75.5 MHz, $CDCl_3$) 32.75, 32.69, 32.57, 31.57, 31.94, 29.31, 22.69, 22.34, 14.09, 12.02, 11.97, and 11.71; δ_{Si} (79.3 MHz, $CDCl_3$) for compound **2.39** -60.95 (SiF, d, *J* 263), -65.11 (**Si**OSiF), -66.00 (SiOSiOSiF), (2:2:4); for compound **2.40** -61.20 (SiF, d, *J* 262), -64.78, -64.83 and -66.50 (1:1:1:1); for compound **2.41** -62.02 (SiF, d, *J* 262) and -64.32 (1:1); for compound **2.42**: -58.16 (SiF, d, *J* 285), -61.47, -65.19 (3:1:3); and others unknown.

4.1.4.3 Reaction of Octaoctylsilsesquioxane with Triflic Acid[13]

Octaoctylsilsesquioxane (0.105 g, 0.08 mmol) was dissolved in $CDCl_3$ (2 ml) in a small vial, to which triflic acid (35 μl) was added. The mixture was allowed to stand at room temperature for 30 minutes, then analysed by ^{29}Si NMR (0.02 g of mixture); δ_H (300 MHz, $CDCl_3$) 1.26 (vbr, m, CH_2), 0.90 (m, CH_3) and 0.64 (Si CH_2); δ_C (75.5 MHz, $CDCl_3$) 118.40 (q, *J* 317 Hz, CF_3), 32.84 (**C**H_2), 32.80 (**C**H_2), 32.60 (**C**H_2), 31.98 (**C**H_2), 31.92 (**C**H_2), 29.35 (**C**H_2), 29.32 (**C**H_2), 29.28 (**C**H_2), 29.25 (**C**H_2), 29.18 (**C**H_2), 22.18 (**C**H_2), 22.54 (**C**H_2), 22.40 (**C**H_2), 22.16 (**C**H_2), 21.72 (**C**H_2), 14.06(**C**H_3), 12.24 (**C**H_3), 12.10 (**C**H_3), 11.94 (**C**H_2Si), 11.47 (**C**H_2Si), 11.74 (**C**H_2Si), 11.53 (**C**H_2Si) and 11.42 (**C**H_2Si); δ_{Si} (79.3 MHz, $CDCl_3$) -60.35, -60.77, -60.92, -61.08, -61.20 (**Si**OTf), -64.61, -64.72, -64.87, -65.01, -65.07, -65.48, -65.65, -66.53.

This reaction mixture was quenched with water (2 × 20 ml), the organic layer was separated and dried with magnesium sulphate. Removal of the solvent gave a colourless

residue. ν_{max} (Neat)/cm^{-1} 3510, 2960, 2931, 2857, 1469, 1409, 1380, 1224, 1187, 1120, 882, 778 and 689; δ_H (300 MHz, $CDCl_3$) 1.25 (vbr, m, CH_2), 0.87 (m, CH_3) and 0.61 (vbr, m, $SiCH_2$); δ_C (75.5 MHz, $CDCl_3$) 32.94 (CH_2), 32.81 (CH_2), 32.70 (CH_2), 32.00 (CH_2), 29.38 (CH_2), 29.33 (CH_2), 29.32 (CH_2), 22.94 (CH_2), 22.84 (CH_2), 22.79 (CH_2), 22.71 (CH_2), 14.09 (CH_3), 12.48 (CH_3), 12.28 (CH_3), 11.72 (CH_2Si) 11.42 (CH_2Si) and 11.21 (CH_2Si); δ_{Si} (79.3 MHz, $CDCl_3$) -55.09, -55.16, -55.27, -55.38 (SiOH), -63.92, -63.97, -64.01, -64.10, -64.97, -65.06, -65.14, -65.40, -65.58, -65.65, -65.73, -65.77, -65.82, -66.08, -66.15, -66.45, -66.73, -67.54, -67.72, -67.82.

4.1.4.4 Rearrangement of Octa-5-phenoxypentylsilsesquioxane using Oxygen Nucleophiles [6]

Octa-5-phenoxypentyl silsesquioxane (0.0825, 0.48 mmol) was refluxed with the base (18.3 mmol) such as sodium acetate potassium hydroxide, sodium hydroxide and sodium trimethylsilanolate in 70ml of dry acetone for 24 hour. The solvent was removed under vacuum and the residue extracted with dichloromethane. After removal of solvent, the residue was analysed by HPLC, NMR, etc.. The HPLC with an ELSD detector was set up in the usual way. The detector conditions were given earlier. A silica 5 μm column was used, and 20 μl of the solution was injected into the instrument for analysis.

4.1.4.5 Rearrangement of Octasilsesquioxanes with TBAF

1) Rearrangement of Octaheptylsilsesquioxane with TBAF

Octaheptylsilsesquioxane (0.13 g, 0.1 mmol) was dissolved in $CDCl_3$ (2 ml). TBAF (1.07 ml of 1 M solution in THF with 5% water) was then added, and the mixture stirred overnight. The reaction mixture was analysed by ^{29}Si NMR spectroscopy. (0.12 g in total, 73% of T_{10} and 10% of T_{12} yield calculated by NMR); ν_{max} (Neat)/cm^{-1} 2961, 2934, 2865, 1499, 1427, 1385, 1263, 1231, 1196, 1126, 1031, 782 and 698; δ_H (300 MHz; $CDCl_3$) 0.41

(vbr, m, CH_2), 0.28 (m, CH_3) and, 0.01 (m, $SiCH_2$); δ_C (75.5 MHz; $CDCl_3$) 31.87, 31.67, 30.90, 22.07, 21.77 (CH_2), 13.08 (CH_3), 11.67 ($SiCH_2$); δ_{Si} (79.3 MHz; $CDCl_3$) -66.64 (**Si** of T_8), -68.38 (**Si** of T_{12}), -68.55 (**Si** of T_{10}) and -70.82 (**Si** of T_{12}).

2) Rearrangement of Octaoctylsilsesquioxane with TBAF

Octaoctylsilsesquioxane (0.5 g, 0.38 mmol) was dissolved in $CDCl_3$ (3 ml). TBAF (3.79 ml of 1 M solution in THF with 5% water) was then added, and the mixture stirred overnight. The reaction mixture was analysed by ^{29}Si NMR spectroscopy. (0.67g in total, 24% of T_8, 65% of T_{10} and 10% of T_{12} yield calculated by NMR); ν_{max} (Neat)/cm^{-1} 2960, 2931, 2864, 1496, 1417, 1380, 1261, 1224, 1194, 1120, 1031, 786 and 697; δ_H (300 MHz; $CDCl_3$) 1.25 (vbr, m, CH_2), 0.81 (m, CH_3) and 0.59 (m, $SiCH_2$); δ_C (75.5 MHz; $CDCl_3$) 33.05, 32.84, 32.64, 31.96, 29.29, 25.57, 25.06, 24.09, 23.09, 22.68, 19.73, 14.05, 13.23, 12.57, 11.92; δ_{Si} (79.3 MHz; $CDCl_3$) -67.38 (**Si** of T_8), -69.05 (**Si** of T_{12}), -69.36 (**Si** of T_{10}) and -71.62 (**Si** of T_{12}); *m/z* (FAB, NOBA matrix) for T_{12}, 1984 (6%, M^+), 1873 (19, M - C_8H_{17}); for T_{10}, 1654 (19%, M + H), 1543 (59%, M - C_8H_{17}); for T_8, 1323 (19%, M + H).

3) Rearrangement of Octanonylsilsesquioxane with TBAF

Octanonylsilsesquioxane (0.75 g, 7.85 mmol) was dissolved in $CHCl_3$ (20 ml). TBAF (7.86 ml of 1 M solution in THF with 5% water) was then added, and the mixture was stirred for 36 hours. The reaction mixture was washed with water (3 × 20 ml), the organic layer was separated and, after removal of the solvent, gave a pale yellow oil product (0.67 g in total, 15% T_8, 73% of T_{12} and 5% of T_{12} yield calculated by NMR); ν_{max} (Neat)/cm^{-1} 2957, 2924, 2855, 1408, 1345, 1284, 1251, 1208, 1122, 1050, 891, 794 and 689; δ_H (300 MHz; $CDCl_3$) 1.24(vbr, m, CH_2), 0.86 (m, CH_3), 0.58 (m, $SiCH_2$); δ_C (75.5 MHz; $CDCl_3$) 32.88, 32.68, 31.97, 29.60, 29.43, 22.98, 22.71(CH_2), 14.08 (CH_3), 12.60 and 11.59 ($SiCH_2$); δ_{Si} (79.3 MHz; $CDCl_3$) -66.63 (**Si** of T_8), -68.11(**Si** of T_{12}), -68.57 (**Si** of T_{10}), -70.84 (**Si** of T_{12}).

4) Rearrangement of Octadecylsilsesquioxane with TBAF

DecylT$_8$ (0.8 g, 0.52 mmol) was dissolved in $CHCl_3$ (10 ml), to which TBAF (7.77 ml of 1 M solution in THF with 5% water) was then added. The mixture was stirred for 36 hours. The reaction mixture was washed with water (3 × 20 ml), the organic layer was separated, and after removal of solvent, gave a yellow oil product. (0.67g in total, 18% of T_8, 66% of T_{10} and 5% of T_{12} yield calculated by NMR); ν_{max} (Nujol)/cm^{-1} 2674, 1408, 1347, 1274, 1110, 1029, 889 and 722; δ_H (300 MHz; $CDCl_3$) 0.36 ($SiCH_2$), 0.88 (CH_3), 1.18 (CH_2); δ_C (75.5 MHz; $CDCl_3$) 14.03, 20.72, 28.75, 29.65, 31.20 and 32.40; δ_{Si} (79.3 MHz; $CDCl_3$) -66.91 (**Si** of T_8), -68.70 (**Si** of T_{12}), -68.82 (**Si** of T_{10}), and -71.10 (**Si** of T_{12}).

5) Rearrangement of Octadodecylsilsesquioxane with TBAF

Octadodecylsilsesquioxane (0.19g, 0.11mmol) was dissolved in $CDCl_3$ (2ml), to which TBAF (1.1ml of 1M solution in THF with 5% water) was then added, and the mixture was stirred 5 and half days. The solvent was removed to give a white solid. This solid was analysed by ^{29}Si NMR spectroscopy. (0.30 g in total, 26% of T_8 and 74% of T_{10} yield calculated by NMR); ν_{max} (Nujol)/cm^{-1} δ_H (300 MHz, $CDCl_3$) 0.25 ($SiCH_2$), 0.81 (CH_3) and 1.08 (CH_2); δ_C (75.5 MHz, $CDCl_3$) 11.94 ($SiCH_2$), 13.38 (CH_3), 22.03 (CH_2), 22.34 (CH_2), 28.76 (CH_2), 28.80 (CH_2), 29.02 (CH_2), 29.08 (CH_2), 29.14 (CH_2), 31.30 (CH_2) and 32.19; δ_{Si} (79.3 MHz; $CDCl_3$) -66.98 for T_8 and -68.92 for T_{10}.

6) Rearrangement of Octacyclohexylsilsesquioxane with TBAF

Octacyclohexylsilsesquioxane (0.2g, 0.18mmol) was dissolved in $CHCl_3$ (20ml). TBAF (1.85ml of 1M solution in THF with 5% water) was then added. The mixture was refluxed for 24 hours, and the solvent was removed to give a white solid. This solid was analysed by ^{29}Si NMR spectroscopy. (0.37 g in total, 82% of CyT_8 and 18% of others yield calculated by NMR); ν_{max} (Nujol)/cm^{-1} 3408, 2667, 1631, 1489, 1270, 1198, 1109, 1028, 892, 849, 826 and 740; δ_H (300 MHz, $CDCl_3$) 0.35 (SiC**H**), 0.67 (C**H$_2$**) and 1.03 (C**H$_2$**); δ_C

(75.5 MHz, $CDCl_3$) 13.20 (SiCH), 24.73 (CH_2) 25.75 (CH_2), 26.56 (CH_2), 27.56 (CH_2) and 28.35 (CH_2); δ_{Si} (79.3 MHz; $CDCl_3$) -68.35, -69.23, -70.24, -70.73, -70.92, -71.04, -71.80, -115.91 ($CySiF_4^-$, quintet, *J* 229); δ_F (376.05 MHz; $CDCl_3$) -121.41.

7) Rearrangement of Octahydrosilsesquioxane with TBAF

The rearrangement reaction of octahydrosilsesquioxane, T_8H_8, with TBAF was carried out in the same way as other octasilsesquioxanes, however, the reaction gave a resin rather than the expected cages.

4.1.6 Synthesis of spherosilicate Compounds

4.1.6.1 Synthesis of Q_8^M, $(SiO_{3/2})_8[OSi(CH_3)_3]_8$

a) Preparation of tetramethylammonium silicate (TMA)

Silicic acid (16.83g, 170 mmol) and tetramethylammonium hydroxide (250 ml of 10% aqueous solution, 274 mmol) were mixed together and stirred overnight at room temperature. The mixture was then heated to 60°C for 10 hours. The mixture was allowed to cool to room temperature, and further cooled to 2°C. The product was recrystallised from distilled water. (26.9 g, 13.9% yield); m.p.: 140.5°C; ν_{max} (Nujol)/cm^{-1} 3402, 2726, 2671, 1665, 1626, 1489, 1153, 1047, 1034, 999, 951, 848 and 712; δ_H (300 MHz, D_2O) 3.14 (96H, s, CH_3); δ_C (75.5 MHz, D_2O) 57.56 (CH_3); δ_{Si} (79.3 MHz, D_2O) -72.48.

b) Synthesis of Q_8^M from tetramethylammonium silicate

A solution of heptane (100ml), dimethylformamide (DMF) (200 ml) and trimethylchlorosilane (100ml, 788 mmol) were mixed together and stirred for 1 hour at room temperature. Tetramethylammonium silicate (4.7g, 4.1 mol) was slowly added to the mixture, and stirred for a further 1 hour. As it is a slightly exothermic reaction, the mixture was allowed to cool to room temperature and then further cooled to 2°C in an ice bath. Water (500 ml) was added to the mixture. The organic layer was separated from the

aqueous layer. The organic layer was then washed with distilled water until it was acid free. The volatiles were removed at 25°C using a rotary evaporator. The resulting liquid was cooled to -20°C and the product precipitated as a white solid, which was recrystallised from acetone.[14, 15] (1.4g, 30.6% yield); m.p 296-297°C; ν_{max} (Nujol)/cm^{-1} 1254, 1089, 868, 843, 756, 723 and 692; δ_H (300 MHz, $CDCl_3$) 0.138 (24H, s, CH_3); δ_C (75.5 MHz, $CDCl_3$) 1.501 (CH_3); δ_{Si} (79.3 MHz, $CDCl_3$) 12.54 (8Si, s, *Si*-CH_3), -108.93 (8Si, s, *Si*-O-$SiCH_3$).

4.1.6.2 Synthesis of Q_6^M, $(SiO_{3/2})_6[(CH_3)_3]_6$

a) Preparation of tetraethylammonium silicate (TEA)

Tetraethylammonium hydroxide (40 ml of 35% in water, 95.2 mmol) was placed in a polyethylene bottle, followed by tetraethoxysilane (20 ml, 89.6 mmol), and the mixture was stirred at room temperature overnight. Then the solvent was removed. A waxy product was obtained. (21.9 g, 84.8% yield); ν_{max} (Nujol)/cm^{-1} 3428, 1668, 1559, 1289, 1105 (SiOSi), 998, 951, 722 and 668; δ_H (300 MHz; CD_3OD) 3.21 (12H, t, *J* 11.34, CH_2) and 1.29 (18H, q, *J* 11.55, CH_3); δ_C (75.5 MHz; CD_3OD) 53.27 (CH_2) and 7.68 (CH).

b) Synthesis of Q_6^M from tetraethylammonium silicate (TEA)

A solution of heptane (500 ml), DMF (200 ml) and trimethylchlorosilane (117 ml, 92 mmol) were mixed together and stirred for 1/2 hour in an ice bath. Then TEA (14 g, 8.1 mmol) was slowly added to the mixture, and stirred for a further 1 hour. As it is a slightly exothermic reaction, the mixture was allowed to warm up to room temperature and then ice water (1 L) was added and the mixture was stirred for a further 1/2 hour. The organic layer was separated from the aqueous layer, and washed with distilled water until acid free. The volatiles were removed at 25°C using a rotary evaporator. A white solid was obtained after recystallisation from actonitrile, to give a colourless crystalline product.[16] (1.96 g, 28.6% yield); m.p.: 120°C; ν_{max} (Nujol)/cm^{-1} 1225, 1078, 846, 814, 759, 730, 644 and 595 and 578; δ_H (300 MHz; $CDCl_3$) 0.17 (54H, s, CH_3); δ_C (75.5 MHz; $CDCl_3$) δ 1.17 (CH_3); δ_{Si}

(79.3 MHz; $CDCl_3$, 0.25 M Cr(acac) solution in $CDCl_3$) 14.29 ($Si(CH_3)_3$), -99.32 ($SiOSi(CH_3)_3$), (1:1); *m/z* (FAB, NOBA matrix) , 847 (M^+), 831, 817, 743, 654, 638, 461, 327 and 147. Full details of the X-ray single crystal structure analysis is shown in the Appendix part 1.

4.1.7 Rearrangement of Octaspherosilicates

4.1.7 1 Rearrangement of Q_8^M with oxygen nucleophiles*

Q_8^M (0.54g, 0.48 mmol) was refluxed with 18.3 mmol of a base, such as sodium acetate potassium hydroxide, sodium hydroxide and sodium trimethylsilanolate, in 70 ml of dry acetone. The solvent was removed under vacuum and the residue extracted with dichloromethane. The dichloromethane was distilled off and the residue was analysed by HPLC, and characterised by NMR. The HPLC with an ELSD detector was set up in the usual way. A PL gel 5µl GPC column was used and HPLC grade toluene as the eluent.

4.1.7.2 Reaction of Q_8^M with electrophiles*

a) Using Triflic Acid

Q_8^M (0.12 g, 0.106 mmol) was dissolved in $CDCl_3$ (2 ml) in a 5 mm NMR tube, to which triflic acid (50 µl) was added. The mixture was allowed to stand at room temperature for 30 minutes, then analysed by ^{29}Si NMR. δ_H (300 MHz, $CDCl_3$) 0.47 ($SiCH_3$) and 0.14 ($SiCH_3$ from the starting material, Q_8^M); δ_C (75.5 MHz, $CDCl_3$) 118.08 (*J* 316.5 MHz, CF_3), 1.18 ($Si(CH_3)_3$) and 0.26 ($SiCH_3$ for the starting material, Q_8^M); δ_{Si} (79.3 MHz, $CDCl_3$) 43.54, 12.69 ($Si(CH_3)_3$).

b) Using HBF_4 and BF_3

Q_8^M (0.502 g, 0.45 mmol) was dissolved in $CDCl_3$ (3 ml) in a 5 mm NMR tube, and then $HBF_4{\cdot}OMe_2$ (250 µl) and $BF_3{\cdot}OEt_2$ (380 µl) was added. The mixture was refluxed for 1.5 hours. This mixture was allowed to stand at room temperature overnight, then washed with

a saturated solution of sodium bicarbonate. The organic layer was separated and dried with magnesium sulphate. A yellow oily product was obtained, after removal of the solvent. δ_H (300 MHz, $CDCl_3$) 0.15 (s, CH_3), and 0.13 (s, CH_3); δ_C (75.5 MHz, $CDCl_3$) 0.19 (CH_3) and 0.74 (CH_3); δ_{Si} (79.3 MHz, $CDCl_3$) 34.87, 31.42, 20.20, 15.81 and -108.08 (t, *J* 322 Hz SiF).

4.1.7.3 Treatment of Q_8^M with TBAF

The rearrangement reaction of Q_8^M using TBAF was carried out in three different ratios 1:3, 1:1 and 1:0.5 of Q_8^M: TBAF. The reaction with a ratio of 1:3 did not yield any peaks in the ^{29}Si NMR, although there were a few peaks in the ^1H and ^{13}C NMR. The reaction at ratio with 1:1 was carried out as follows: Q_8^M (1.75 g, 1.55 mmol) was dissolved in dry CH_2Cl_2 (50 ml), to which TBAF (15.5 ml of 1 M solution in THF with 5% water) was added. The mixture was stirred at room temperature overnight. The mixture was worked up in the usual way with water, however, copious amount of a white solid were obtained on adding the water. The organic layer containing the white solid was separated, and after filtration, gave a white solid (0.11 g), which did not dissolved in any common solvents. After filtration of the organic layer, the filtrate liquid was collected, and the solvent removed to give a colourless liquid residue. (0.1 g, 90%yield calculated by NMR); ν_{max} (Nujol)/cm^{-1} 1246, 1201, 1060, 838 and 756; δ_H (300 MHz, $CDCl_3$) 0.06 (s, CH_3); δ_C (75.5 MHz, $CDCl_3$) 1.43 (s, CH_3); δ_{Si} (79.3 MHz, $CDCl_3$) 8.35 ($Si(CH_3)_3$) and 104.64 (O-Si-O). The reaction at ratio with a ratio 1:0.5 was carried out using the same procedure as before. However, NMR shows a complex ^1H and ^{13}C and no peak in ^{29}Si NMR.

4.1.7.4 Treatment of Q_6^M with TBAF in a ratio of 1:0.5

Q_6^M (0.0418 g, 0.025 mmol) was dissolved in $CDCl_3$ (1 ml), then excess of TBAF (24.7 µl of 1 M solution in THF with 5% water) was added. The mixture was stirred at room

temperature for 5 minutes, then analysed by ^{29}Si NMR. NMR shows the reaction failed to give well-defined cages.

4.2. Synthesis and Rearrangement of Hexasilsesquioxane Cages

4.2.1 Synthesis of Hexasilsesquioxane Cages

4.2.2.1 Synthesis of Hexacyclohexylsilsesquioxane 3.1, CyT_6, $(c\text{-}C_6H_{11})_6Si_6O_9$)

Hexacyclohexylsilsesquioxane was prepared according to the method of Bassindale or Feher.[5,17]

a) Hydrolysis at Room Temperature[1,18]

Anhydrous iron chloride (30 g, 185 mmol) and concentrated hydrochloric acid (12 ml) were added to a 2 L round bottom flask, followed by methanol (25 ml), hexane (400 ml) and toluene (30 ml). The mixture was stirred using a magnetic stirrer for half an hour. A solution of cyclohexyltrichlorosilane (25 g, 114 mmol) in hexane (150 ml) was added drop-wise using a pressure equalising funnel, over a period of six and half hours. The reaction mixture was carried on stirring for a further half an hour. The upper hexane layer was transferred into another 2 L round bottom flask. Sodium carbonate (28 g, 264 mmol) and calcium chloride (20 g, 180 mmol) were added to the mixture and stirring continued overnight. After filtration, the solvent was removed using a rotary evaporator. A fine white solid was produced. This solid was recrystallised from hexane to give the pure product as a white crystalline solid (2.4 g, 15.9% yield); m.p.: 265-266°C; (literature: m.p.: 266°C); ν_{max} (Nujol)/cm^{-1} 2656 (C-H), 1283, 1201, 1090, 1053, 897, 860, 778, 764 and 641; δ_H (300 MHz; $CDCl_3$) 1.99 (24H, vbr, m), 1.66 (36H, vbr, m) and 0.77 (6H, vbr, m, SiH); δ_C (75.5 MHz; $CDCl_3$) 27.28, 26.16 (CH_2) and 22.65 (SiCH); δ_{Si} (79.3 MHz; $CDCl_3$) -56.60; *m/z* (EI) 811.4 (20%, M + H), 728 (28%, M^+-C_6H_{11}).

b) Hydrolysis at High Temperature[19]

Cyclohexyltrichlorosilane (75 g, 345 mmol) was dissolved in acetone (1.5 L), to which water (450 ml) was added cautiously. The mixture was refluxed for 65 hours, then the mixture was allowed to cool down to room temperature and filtered. A white solid with a yellow oily gel was obtained. This mixture was washed with acetone (3 × 50 ml) to give hexacyclohexylsilsesquioxane, CyT_6, (12.96 g, 27.8% yield) as a white solid, m.p.: 266°C; ν_{max} (Nujol)/cm^{-1} 2656, 1283, 1201, 1090, 1053, 897, 860, 778, 764 and 641; δ_H (300 MHz; $CDCl_3$) 1.99 (24H, vbr, m), 1.66 (36H, vbr, m) and 0.77 (6H, vbr, m, SiH); δ_C (75.5 MHz; $CDCl_3$) 27.28, 26.16 (CH_2) and 22.65 (SiCH); δ_{Si} (79.3 MHz; $CDCl_3$) -56.60; *m/z* (EI) 811.4 (20%, M + H), 728, 647, 565, 483, 397, 317, 165 and 81.

4.2.1.2. Synthesis of Hexacyclopentylsilsesquioxane 3.4, CpT_6, $(c\text{-}C_5H_9)_6Si_6O_9$[1,18]

Anhydrous iron chloride (66 g, 406 mmol), and concentrated hydrochloric acid (26 ml) were added to a 2 L round bottom flask, followed by methanol (55 ml), hexane (600 ml) and toluene (100 ml). The mixture was stirred using a magnetic stirrer for half an hour. A solution of cyclopentyltrichlorosilane (50 ml, 301 mmol) in hexane (300 ml) was added dropwise using a pressure equalising funnel, over a period of 8 hours. After additional overnight stirring, the upper hexane layer was transferred to 2 L round bottom flask. Sodium carbonate (28 g) and calcium chloride (20 g) were added to the flask and stirring continued overnight. After filtration, the filtrate was collected and the solvent removed using a rotary evaporator to give a yellow residue. Recrystallisation of this residue in hexane gave a cubic crystalline product, CpT_6. (6.5 g, 17.8% yield); m.p.: 154°C; ν_{max} (Nujol)/cm^{-1} 2767, 2667, 1239, 1083, 919, 778, 741 and 660; δ_H (300 MHz; $CDCl_3$) 1.75 (12H, vbr, m,), 1.51 (36H, vbr, m) and 1.06 (6H, vbr, m); δ_C (75.5 MHz; $CDCl_3$) 27.00, 26.82 (CH_2) and 21.70 (CH); δ_{Si} (79.3 MHz; $CDCl_3$) -54.36; *m/z* (FAB): 727 (11%, M + H^+). The X-ray crystal structure was obtained and full details are given in Appendix part 2.

4.2.1.3. Synthesis of Hexa-*iso*-butysilsesquioxane 3.5c*

Hexa-*iso*-butysilsesquioxane was prepared according to Maesano's method [20]and modified. Dimethylsulphoxide, DMSO (13.39 g, 171 mmol) was dissolved in chlorofrom (120 ml) to which a solution of *iso*-butyltrichlorosilane (16 g, 83.5 mmol) in chloroform (120 ml) was added dropwise. The mixture was stirred overnight, and the solvent removed at 30°C using a rotary evaporator. A colourless oily residue was obtained. This crude product was purified by flash chromatography using an alumina column with hexane: chloroform 1:1, followed by a silica column chromatography with chloroform to yield a waxy product of *iso*-butylT_6 (1.75 g, 19.2% yield); m.p.: 30-32°C; ν_{max} (Nujol)/cm^{-1} 2871, 2731, 2626, 1597, 1367, 1334, 1229, 1083, 1051, 954, 922, 896, 840, 815, 785, 741, 699 and 683; δ_H (300 MHz; $CDCl_3$) 1.52 (6H, Sept, C**H**), 0.60 (36H, d, CH_3) and 0.26 (12H, d, CH_2); δ_C (75.5 MHz; $CDCl_3$) 25.71 (CH_3), 23.72 (**C**H), 22.62 (CH_2); δ_{Si} (79.3 MHz; $CDCl_3$) -55.38; *m/z* (EI) 654 (M^+), 639, 597, 583, 541, 485 and 56.

4.2.1.4 Synthesis of hexaoctylsilsesquioxane 3.5d*

Hexaoctylsilsesquioxane was prepared according to Maesano's method[20] A solution of octyltrichlorosilane (24.7 g, 100 mmol) in chloroform (200 ml) was added dropwise to a solution of dimethylsulphoxide (15.63 g, 200 mmol) was dissolved in chloroform (200 ml). The mixture was stirred overnight, and then this mixture was washed with water (10 × 300 ml) and the organic layer was separated to give an oily residue after removal of solvent. The residue was recrystallised from a mixed solvent of chloroform and acetone (1:2) to yield a pure product of OctylT_6 (0.7 g, 4.2% yield); m.p.: 42-44°C; ν_{max} (Nujol)/cm^{-1} 2729, 2672, 1303, 1273, 1233, 1186, 1054, 721 and 689; δ_H (300 MHz; $CDCl_3$) 1.25 (72H, vbr, m, CH_2), 0.86 (18H, vbr, m, CH_3) and 0.67 (16H, vbr, m, SiCH_2); δ_C (75.5 MHz; $CDCl_3$) 32.56, 31.91, 29.23, 22.65, 22.29(CH_2), 14.07 (CH_3) and 11.32 (SiCH_2); δ_{Si} (79.3 MHz;

$CDCl_3$) -54.18; *m/z* (FAB) 991 (35%, M + H), 960, 905, 685, 663, 396, 946, 315, 178 and 145.

4.2.1.5 Synthesis of Hexa-*p*-methoxyphenylpropylsilsesquioxane 3.5e*

Hexa-*p*-methoxyphenylpropylsilsesquioxane was prepared according to Maesano's method[20] Dimethylsulphoxide, DMSO (13.7 g, 176 mmol) was dissolved in chloroform (350 ml), then a solution of *p*-methoxyphenylpropyltrichlorosilane (50 g, 176 mmol) in chloroform (150 ml) was added to the mixture very slowly. This mixture was stirred at room temperature for 24 hours to give a yellow gel residue after removal of the solvent. This residue was washed with acetone (3 × 100 ml). A white solid was obtained after filtration, which could be recrystallised from a mixture of hexane and chloroform (2:1). (4.44 g, 12.5% yield); m.p.: 139°C; ν_{max} (Nujol)/cm^{-1} 2727, 1612, 1584, 1513, 1402, 1321, 1302, 1244, 1187, 1176, 1125, 1098, 1046, 1006, 850, 824, 812, 782, 749, 735, 722 and 680; δ_H (300 MHz; $CDCl_3$) 0.71 (12H, t, *J* 16.11, $SiCH_2$), 1.71 (12H, quintet, *J* 7.71, $SiCH_2CH_2$), 2.56 (12H, t, *J* 7.5, $SiCH_2CH_2CH_2$), 3.78 (18H, s, OCH_3), 6.77 (12H, d, *J* 8.61, CH of Ar), 7.02 (12H, d, *J* 8.61, CH of Ar); δ_C (75.5 MHz; $CDCl_3$) 10.93 ($SiCH_2$), 24.34 ($SiCH_2CH_2$), 37.57 ($SiCH_2CH_2CH_2$), 55.19 (OCH_3), 113.66 (CH of Ar) 129.31 (CH of Ar), 134.08 (CCH_2 of Ar) and 157.71 ($COCH_3$); δ_{Si} (79.3 MHz; $CDCl_3$) -54.42. Full details of the X-ray Crystallographic analysis is shown in Appendix part 3.

4.2.2. Rearrangement of Hexasilsesquioxane cages

4.2.2.1 Rearrangement of Hexacyclohexylsilsesquioxane using eletrophiles

c) Using HBF_4/BF_3

The reaction of hexacyclohexylsilsesquioxane with HBF_4/BF_3 was carried out as a "Stack Experiment". CyT_6 (0.1067 g, 0.1317 mmol) was dissolved in 2 ml of deuterium chloroform in a 5 nm NMR tube followed by $HBF_4{\cdot}OMe_2$ (74 µl, 0.61 mmol) and $BF_3{\cdot}OEt_2$

(98 μl, 0.79 mmol).[21] The mixture was carried out a "Stack Experiment" overnight. The ^{29}Si NMR spectra were collected each hour for a period of 15 hours.

d) Using Triflic acid, TfOH

The reaction of CyT_6 with TfOH was carried out in a ratio 1:5 of CyT_6: TfOH in different solvent system, such as deuterated chloroform[22] and benzene.

a) Using deuterated chloroform as solvent

CyT_6 (0.1075 g) was dissolved in $CDCl_3$ (2 ml) in a small vial, and then triflic acid (58 μl) was added. The mixture was allowed to stand at room temperature for 30 minutes, and then analysed by NMR. δ_H (300 MHz; $CDCl_3$) 1.23 (m, vbr, CH_2), 0.75 (m, vbr, CH_2) and 0.41 (m, vbr, $SiCH_2$), δ_C (75.5 MHz; $CDCl_3$) 27.15, 27.05, 26.82, 26.64, 26.24, 26.08, 25.66, 25.42, 25.00, 22.86, 22.64, 22.42, 22.00 and 21.91; δ_{Si} (79.3 MHz; $CDCl_3$) -55.80, -56.08, -60.22, -61.08, -61.44, -63.80, -65.24, -66.31, -67.25, -68.16 and -68.64.

b) Using C_6D_6 as solvent

The reaction of CyT_6 with triflic acid in C_6D_6 was carried out in the same way as using $CDCl_3$. However, the reactions gave different outcomes, which were difficult to characterise.

4.2.2.2 Rearrangement of Hexasilsesquioxane using Oxygen Nucleophiles[6]

The reaction was carried out according to the method of Marsmann and co-workers.

e) Using Sodium Acetate

CyT_6 (0.5 g, 0.67 mmol) was dissolved in dry dichloromethane (15 ml) to which sodium acetate (1.22 g, 1.23 mmol) and acetone (50 ml) was added. The mixture was refluxed and analysed by NMR spectroscopy after 5 hours. The mixture was refluxed for a further 24 hours. Then the mixture was washed with sodium bicarbonate (saturated solution), the

organic layer was separated and the solvent removed by rotary evaporator to give the starting material.

f) Using Potassium Carbonate

CyT_6 (0.5 g, 0.62 mmol) was dissolved in dry chloroform (5 ml), to which potassium carbonate (1.70 g, 12.3 mmol) and acetone (100 ml) was added. The mixture was refluxed for 3 days. The organic layer was separated and the solvent removed by rotary evaporator to give an oily mixture (0.24 g mixture); ν_{max} (Nujol)/cm^{-1} 2723, 2671, 1751, 1305, 1268, 1201, 1053, 897, 845, 816 and 756; δ_H (300 MHz, $CDCl_3$) 1.72 (vbr, m, CH_2), 1.24 (vbr, m, CH_2) and 0.71 (vbr, m, SiCH); δ_C (75.5 MHz, $CDCl_3$) 27.50 (CH_2), 27.22 (CH_2), 26.73 (CH_2), 26.57 (CH_2) 26.10 (CH_2) and 22.60 (SiCH); δ_{Si} (79.3 MHz, $CDCl_3$) -21.90, -67.88, -68.71, -70.15, -70.36; *m/z* (MALDI-TOF, DHB matrix) (100%, M^+ + Ag, 970), (32, M + Ag^+, 1603).

g) Using Sodium trimethylsilanoate

CyT_6, (0.3 g, 0.37 mmol) was dissolved in dry dichloromethane (50 ml) to which sodium trimethylsilanoate (2.5 ml of 1 M solution in dichloromethane) was added. The mixture was refluxed for 48 hours. Then the mixture was washed with saturated solution of sodium bicarbonate, the organic layer was separated and the solvent removed by rotary evaporator to give a yellow oily residue (0.28 g mixture); ν_{max} (Neat)/cm^{-1} 2931, 2849, 1439, 1253, 1194, 1112, 1053, 897, 838 and 756; δ_H (300 MHz, $CDCl_3$) 1.92 (vbr, m, CH_2), 1.28 (vbr, m, CH_2), 0.84 (vbr, m, SiCH) and 0.14 (m, CH_3); δ_C (75.5 MHz, $CDCl_3$) 29.14 (CH_2), 27.88 (CH_2), 27.10 (CH_2), 25.36 (CH_2), 24.96(CH_2), 22.74 (CH_2), 20.52 (SiCH), 18.83 (SiCH), 14.38 (SiCH), 14.18 (SiCH), 11.49 ($SiCH_3$), 1.99 ($SiCH_3$) and 1.88 ($SiCH_3$); δ_{Si} (79.3 MHz, $CDCl_3$) 8.27 ($Si(CH_3)_3$), 7.85 ($Si(CH_3)_3$), 7.71 ($Si(CH_3)_3$), 7.38 ($Si(CH_3)_3$), 6.89 ($Si(CH_3)_3$), 6.74 ($Si(CH_3)_3$), -67.18 (SiOSi), -69.75 (SiOSi), -70.82 (SiOSi), -71.08 (SiOSi), -71.11 (SiOSi), -72.94 (SiOSi).

4.2.2.3 Rearrangement of Hexasilsesquioxanes using Lewis acids[23]

Aluminium chloride and iron chloride was used as Lewis acids in the rearrangement of hexacyclohexylsilsesquioxane, CyT_6. The reaction was carried out with 5% of the Lewis acid at room temperature and also at reflux. However, no reaction occurred and only the starting material was observed at the end.

4.2.2.4 Using TBAF

1) Rearrangement of Hexacyclohexylsilsesquioxane

a) Rearrangement of CyT_6 with TBAF in a ratio of 1:2 in molar

CyT_6 (0.31 g, 0.3 mmol) was dissolved in deuterated chloroform (5 ml) and TBAF (0.8 ml of 1 M solution in THF with 5% water) was added. The mixture was stirred at room temperature overnight, Then washed with sodium bicarbonate (saturated solution, 3 × 50 ml) and the organic layer was separated and dried with magnesium sulphate. Removal of the solvent gave a white solid product, which could be recrystallised from hot chloroform to give a pure CyT_8 (0.15 g, 34.7% yield); m.p.: < 400°C (dec.); ν_{max} (Nujol)/cm^{-1} 2851, 2667, 1652, 1557, 1539, 1348, 1269, 1197, 1111, 1039, 1027, 999, 895, 849, 827 and 724; δ_H (300 MHz; $CDCl_3$) 1.71 (48H, vbr, m), 1.22 (32H, vbr, m) and 0.77 (8H vbr, m); δ_C (75.5 MHz; $CDCl_3$) 27.28, 26.62 (CH_2) and 22.65 (SiCH); δ_{Si} (79.3 MHz; $CDCl_3$) -68.69; *m/z* (EI), $C_{48}H_{88}Si_8O_{12}$, 996 (80%, M^+-C_6H_{11}), 914, 833, 751, 423 and 81.

2) Controlling the Rearrangement of Hexasilsesquioxanes

a) Monitoring the reaction using ^{29}Si NMR spectroscopy

Two "stack experiments" were carried for monitoring the reaction of CyT_6 with TBAF using ^{29}Si NMR spectroscopy. The first "stack experiment" was carried out using TBAF with a ratio 1:2 of CyT_6: TBAF. Thus CyT_6, (0.0245 g, 0.60 mmol) was dissolved in deuterated chloroform (1 ml) in a 5mm NMR tube, to which TBAF (60 μl of 1M solution

in THF with 5% water) was added. The mixture was stirred for 1 minute and analysed by ^{29}Si NMR spectroscopy. The NMR spectrum was collected every hour over a 50 hours period. The second "Stack Experiments" was carried out with the same procedure as the first one, but using a ratio 1:0.5 of CyT_6: TBAF. The NMR spectra were collected every 2 hours over a 16 hours period.

Controlling the reaction after 4 hours

CyT_6 (10 g, 12 mmol) was dissolved in chloroform (200 ml), to which TBAF (6.2 ml of 1M solution in THF with 5% water) was added. The mixture was stirred for 4 hours, then washed with water (3 × 300 ml). The organic layer was separated and dried with magnesium. Removal of the solvent gave a white solid. This mixture was separated by fraction of recrystallisation from different solvents, hexane, chloroform, and acetone.

The first fraction was collected from hot hexane to give the pure product, $CyT_7(OH)_3$, **3.15** (0.37 g, 2.6% yield); m.p.: 250°C (dec.); ν_{max} (Nujor)/cm^{-1} 3583 (vbr, s, OH), 2727, 2666, 2361, 1268, 1195, 1113, 1038, 999, 893, 826, 786 and 740; δ_H (300 MHz; $CDCl_3$) 6.92 (3H, vbr, s, SiOH), 1.74 (35H, vbr, m, CH_2), 1.26 (vbr, m, 35H, CH_2) and 0.74 (7H, vbr, m, SiCH); δ_C (75.5 MHz; $CDCl_3$) 27.53, 26.90,26.64 (s, 2:1:2, CH_2), 23.89, 23.54, 23.10(s, 3:3:1, CH); δ_{Si} (79.3 MHz, $CDCl_3$) -60.53, -68.25, -69.84 (3:1:3); *m/z* (FAB) 973 (34%, M + H).

The second fraction was obtained from hexane/chloroform (9:1) to give CyT_8, (0.74 g, 7.3% yield); m.p.: < 400°C (dec.); 2851, 2667, 1652, 1557, 1539, 1348, 1269, 1197, 1111, 1039, 1027, 999, 895, 849, 827 and 724; δ_H (300 MHz; $CDCl_3$) 1.73 (48H, vbr, m), 1.15 (32H, vbr, m) and 0.83 (8H vbr, m); δ_C (75.5 MHz; $CDCl_3$) 27.55, 26.86 (CH_2) and 23.89 (SiCH); δ_{Si} (79.3 MHz; $CDCl_3$) -68.69.

Fraction 3 was obtained from recrystallisation of the remaining residue from chloroform/acetone (5:5) to give CyT_9OH. **3.13*** (1.25 g, 12.4%); m.p.: 203°C; ν_{max}

(Nujol)/cm^{-1} 3696, 2726, 2667, 1655, 1328, 1276, 1197, 1112, 1039, 1027, 999, 913, 895, 849, 826, and 740; δ_H (300 MHz; $CDCl_3$) 2.34 (1H, vbr, s, **OH**), 1.66 (45H, vbr, m, $\mathbf{CH_2}$), 1.15 (45H, vbr, m, $\mathbf{CH_2}$) and 0.83 (9H, vbr, m, Si**CH**); δ_C (75.5 MHz; $CDCl_3$) 27.55, 27.52, 27.40, 26.86, 26.77, 26.62, 26.51, 23.71, 23.67($\mathbf{CH_2}$), 23.95, 23.57, 23.04 and 22.64(**CH**); δ_{Si} (79.3 MHz; $CDCl_3$) -59.27 (**Si**OH), -67.81, -70.04, -70.32 and -70.60 (**Si**CH), (1:2:2:2:2); *m/z* d 1226 (7%, M + H), 1208, 1441, 1057, 991, 766, 391 and 124. The X-ray crystal structure was obtained and is shown in Appendix part 4.

c) Silylation of CyT_9OH 3.14*

CyT_9OH (2.95 g, 2.4 mmol) was dissolved in chloroform (20 ml), to which trimethylchlorosilane, TMSCl, (30 ml, 236 mmol) was added, and the mixture was stirred at room temperature for 4 hours. The volatiles were removed using a rotary evaporator at 30°C. A white residue was obtained, which can be recystallised from hexane to give the pure product CyT_9OTMS. (3.00 g, 96.2% yield); m.p.: 295-298°C; ν_{max} (Nujol)/cm^{-1} 2726, 2666, 1654, 1461, 1269, 1197, 1111, 1027, 895, 849, 827, and 724; δ_H (300 MHz; $CDCl_3$) 1.51 (45H, vbr, m, $\mathbf{CH_2}$), 1.19 (45H, vbr, m, $\mathbf{CH_2}$), 0.56 (9H, vbr, m, Si**CH**) and 0.08 (9H, s, $\mathbf{CH_3}$); δ_C (75.5 MHz; $CDCl_3$) 27.73, 27.69, 27.62, 27.04, 26.95, 26.89, 26.67 ($\mathbf{CH_2}$), 24.34, 24.27, 23.90, 23.85, 23.23 (**CH**) and 1.77 ($\mathbf{CH_3}$); δ_{Si} (79.3 MHz; $CDCl_3$) -68.03, -68.99 (**Si**$(CH_3)_3$), -70.45, -70.75 and -71.71 (**Si**C_6H_{11}), (1:2:2:2:2); *m/z* (EI) 1281 (0.4%, $M^+ - CH_3$), 1214, 1212, 1130, 1048, 915, 833, 750 and 81; Found: C, 52.42; H, 8.45. $C_{57}H_{108}O_{14}Si_{10}$ requires C, 52.73; H, 8.38%. Full details of the X-ray crystal structure are shown in Appendix part 5.

d) ^{29}Si NMR stack experiments of CyT_9OH*

CyT_9OH (0.0279 g, 0.024 mmol) was dissolved in deuterated chloroform (0.5 ml) in a 5mm NMR tube to which TBAF (12.1 μl of 1M solution in THF with 5% water) was added. The mixture was stirred for 1 minute and then $Cr(acac)_3$ (0.5 ml of 0.025M solution

in $CDCl_3$) was added. The mixture was analysed by ^{29}Si NMR spectroscopy, the data was collected for every 3 hours over a 15 hours period. Then, the mixture was allowed to stand at room temperature for a further 24 hours. TBAF (12.1 μl of 1M solution in THF with 5% water) was added and the stack experiment repeated, and data again were collected for every 3 hours over a 15 hour period.

e) Monitoring the reaction using HPLC

CyT_6 (0.5005 g, 0.62 mmol) was dissolved in chloroform (10 ml) to which TBAF (308 μl of 1M solution in THF with 5% water) was added. The reaction was stirred at room temperature, and the reaction mixture was analysed by HPLC every 30 minutes over 10 hours. After this, the mixture was stirred for a further 22 hours, and analysed again after 28 hour, 29 hours and 30 hours.

The HPLC with ELSD detector was set up as usual. The column used was a silica 5 μm column. Chloroform and *iso*-octane were used as the eluent, and the solvent system was controlled as a gradient, shorting with 30% chloroform in *iso*-Octane was run for 5 min, then the proportion of chloroform increased to 100% over 15 min, and held there for 10 min.

4.2.2.5 Rearrangement of Partial Silsesquioxanes with TBAF

1) Synthesis of Partial Silsesquioxanes

a) Synthesis of Cyclohexyltetrol[24]

Cyclohexyltetrol, $CyT_6(OH)_4$, was prepared according to Feher's method. CyT_6 (2.2 g, 0.25 mmol) and THF (25 ml) was placed in a flask to which tetraethylammonium hydroxide (1 ml of 35% solution in water) was added, and the mixture was stirred for 1 hour. The mixture was neutralised using diluted solution of hydrochloric acid and the organic layer was separated to give a white solid after removal of the solvent. The pure product was

obtained by recrystallisation from THF. (1.60 g, 78.9% yield); δ_H (300 MHz, $CDCl_3$) 6.23 (4H, vbr, s, **OH**), 1.83 (30H, vbr, m, $\mathbf{CH_2}$), 1.21 (30H, vbr, m, $\mathbf{CH_2}$), 0.72 (6H, vbr, m, **CH**); δ_C (75.5 MHz, $CDCl_3$) 27.52 ($\mathbf{CH_2}$), 27.43 ($\mathbf{CH_2}$), 26.82 ($\mathbf{CH_2}$), 26.59 ($\mathbf{CH_2}$), 25.55 ($\mathbf{CH_2}$), 23.66 (**CH**) and 23.12 (**CH**); δ_{Si} (79.3 MHz, $CDCl_3$) -59.55 (**Si**OH) and -68.88 ($\mathbf{Si}OSiC_6H_{11}$), (2:1).

b) Synthesis of Cyclohexyltriol

Cyclohexyltriol, $CyT_7(OH)_3$ was synthesised by the rearrangement reaction of CyT_6 using TBAF, and controlling the reaction time at 4 hours to give $CyT_7(OH)_3$, as described in the previous section.

c) Synthesis of Cyclohexylol*

Cyclohexylol, CyT_9OH, was synthesised from the rearrangement reaction of CyT_6 using TBAF, and controlling the reaction time at 4 hours to give CyT_9OH, as described in the previous section.

2) Rearrangement of Partial Silsesquioxanes using TBAF

a) Rearrangement of Cyclohexyltetrol*

Cyclohexyltetrol, $CyT_6(OH)_4$ (0.20 g, 0.24 mmol) was dissolved in deuterated chloroform (2 ml) to which TBAF (118µl of 1 M solution in THF with 5% water) was added. The mixture was stirred at room temperature overnight. A white solid precipitated out, which after filtration gave a white solid of CyT_8. (0.18 g, 52.1% yield); δ_H (300 MHz; $CDCl_3$) 1.73 (48H, vbr, m), 1.15 (32H, vbr, m) and 0.83 (8H vbr, m); δ_C (75.5 MHz; $CDCl_3$) 27.55, 26.86 ($\mathbf{CH_2}$) and 23.89 (Si**C**H); δ_{Si} (79.3 MHz; $CDCl_3$) -68.69.

b) Rearrangement of $CyT_7(OH)_3$*

$CyT_7(OH)_3$ (0.12 g, 0.12 mmol) was dissolved in dry deuterated chloroform (2 ml), to which TBAF (61.7μl of 1 M solution in THF with 5% water) was added. The mixture was stirred at room temperature overnight, and then the mixture was worked up in the usual way with water. However, copious amount of a white solid precipitated out when adding the water. The organic layer with white solid was separated to give a white solid after filtration. NMR analysis showed this product was a mixture of CyT_8 and CyT_9OH from. δ_H (300 MHz; $CDCl_3$) 1.73 (m, vbr, SiCH), 1.15 (m, vbr, CH_2) and 0.83 (m, vbr, CH_2); δ_C (75.5 MHz; $CDCl_3$) 27.55, 26.86 ($\mathbf{C}H_2$) and 23.89 (Si**C**H); δ_{Si} (79.3 MHz, $CDCl_3$) -59.61, -67.92, -68.71, -70.27, -70.39, -70.89

4.2.2.6 Rearrangement of Hexacyclopentylsilsesquioxane

1) Complete Rearrangement

CpT_6, (0.32 g, 0.44 mmol) was dissolved in deuterated chloroform (5 ml), and then TBAF (881 μl of 1 M solution in THF with 5% water) was added. The mixture was stirred at room temperature overnight. A solid precipitated out, and after filtration gave the product as octacyclopentylsilsesquioxane, CpT_8, (0.13 g, 22.9% yield); m.p.: < 400°C (dec.); ν_{max} (Nujol)/cm^{-1} 2726, 1655, 1323, 1249, 1110, 949, 914 and 723; δ_H (300 MHz; $CDCl_3$) 1.72 (16H, vbr, m), 1.51 (48H, vbr, m) and 0.77 (8H, vbr, m); δ_C (75.5 MHz; $CDCl_3$) 27.30, 27.02 (CH_2), 22.26 (Si**C**H); δ_{Si} (79.3 MHz; $CDCl_3$) -66.57.

2) Controlled reaction of Hexacyclopentylsilsesquioxane with TBAF after 3 hours

CpT_6, (3.0 g, 4.13 mmol) was dissolved in chloroform (100 ml), to which TBAF (2.07 ml of 1 M solution in THF with 5% water) was added. The mixture was stirred for 3 hours, then washed with water (4 × 200 ml). The organic layer was separated and dried with

magnesium sulphate, and after removal of solvent gave a white solid. This solid mixture was separated by fractional recrystallization from different solvents, hexane, chloroform, and acetone.

Fraction 1 was collected from hexane to give a pure product of $CpT_7(OH)_3$ (0.16 g, 5.2% yield); m.p.: < 400°C (dec.); ν_{max} (Nujol)/cm^{-1} 3172, 1323, 1246, 1104, 921, 877 and 722; δ_H (300 MHz; $CDCl_3$) 6.29 (3H, s, **OH**), 1.59 (14H, vbr, m), 1.34 (42H, vbr, m) and 1.10 (7H, vbr, m); δ_C (75.5 MHz; $CDCl_3$) 25.85, 25.72, 23.87 (**CH_2**), 23.62, 23.11, 22.41 (**CH**); δ_{Si} (79.3 MHz; $CDCl_3$) -57.72 (**SiOH**), -66.03, -67.44 (3:1:3)

Fraction 2* was collected from the recrystallisation of the rest of the residue from hot hexane to give CpT_9OH. (0.21 g, 7.1% yield); ν_{max} (Nujol)/cm^{-1} 3198, 1323, 1295, 1246, 1121, 915 and 723; δ_H (300 MHz; $CDCl_3$) 2.40 (1H, vbr, s, **OH**), 1.77 (18H, vbr, m, **CH_2**), 1.40 (54H, vbr, m, **CH_2**), 0.96 (9H, vbr, m, **CH**); δ_C (75.5 MHz; $CDCl_3$) 27.44, 27.37, 27.33, 27.31, 27.21,26.98, 26.96(**CH_2**), 23.15, 22.64, 22.42, 22.23 (**CH**); δ_{Si} (79.3 MHz; $CDCl_3$) -57.39 (**SiOH**), -65.63, -67.92, -68.23, -68.58 (1:2:2:2:2).

Faction 3* was collected from extraction of hot hexane, $CpT_6(OH)_4$. δ_H (300 MHz; $CDCl_3$) 6.41 (4H, vbr, s, **OH**), 1.75 (12H, vbr, m), 1.03 (36H, vbr, m) and 0.99 (6H, vbr, m); δ_C (75.5 MHz; $CDCl_3$) 27.30, 27.28 (**CH_2**) and 22.27 (**CH**); δ_{Si} (79.3 MHz; $CDCl_3$) -57.525 (**SiOH**), 66.79 (2:1); *m/z* (Electrospray) 763 (100%, M), 743, 763, 338 and 282.

Fraction 4 CpT_8, (0.5, 16.7% yield); m.p.: < 400°C (dec.); ν_{max} (Nujol)/cm^{-1} 3181, 1324, 1298, 1248, 1116, 894, 876 and 723; δ_H (300 MHz; $CDCl_3$) 1.67 (16H, vbr, m, **CH_2**), 1.44 (48H, vbr, m, CH_2) and 0.96 (8H, vbr, m, **CH**); δ_C (75.5 MHz; $CDCl_3$) 27.40, 27.11 (**CH_2**), 22.56(**CH**); δ_{Si} (79.3 MHz; $CDCl_3$) -67.55; *m/z* (EI) 899 (100%, M - C_5H_9), 830, 762, 695, 627, 559, 489, 423, 354 and 67.

4.2.2.7 Rearrangement of Hexa-*iso*-butysilsesquioxane*

TBAF (0.78 ml of 1 M solution in THF with 5% water) was added to *iso*-butylT_6, (1.03 g, 1.57 mmol) which dissolved in chloroform (20 ml). The mixture was stirred for 2 hours, then washed with water (3 × 30 ml). The organic layer was separated and dried with magnesium sulphate. Removal of the solvent gave a white solid. This white solid mixture was separated by chromatography using silica-gel column with chloroform: hexane (1:1) as the eluent, to yield the first product, *iso*-butylT_8. (0.20 g, 39.2% yield); m.p.: 268°C; ν_{max} (Nujol)/cm^{-1} 2728, 2626, 1399, 1367, 1332, 1230, 1208, 1169, 1117, 1039, 955, 838, 806 and 748; δ_H (300 MHz; $CDCl_3$) 1.90 (8H, sept, *J* 12, **CH**), 0.93 (48H, d, *J* 18, CH_3) and 0.565 (16H, d, *J* 9, CH_2); δ_C (75.5 MHz; $CDCl_3$) 25.83 (**C**H_3), 23.87 (**C**H) and 22.53(Si**C**H_2); δ_{Si} (79.3 MHz; $CDCl_3$) δ -67.90; *m/z* (MALDI-TOF, DHB matrix) 873.56 (100%, M).

The second oily product was obtained, *iso*-butylT_9OH (0.9 g, 40% yield); ν_{max} (Nujol)/cm^{-1} 3505, 2871, 2718, 2627, 1430, 1402, 1383, 1333, 1261, 1229, 1121, 955, 920, 838, 801 and 742; δ_H (300 MHz; $CDCl_3$) 1.89 (9H, sept, *J* 9 **CH**), 0.93 (54H, d, *J* 9 CH_3) and 0.41 (18H, d, *J* 6 CH_2); δ_C (75.5 MHz; $CDCl_3$) 29.18 (**C**H_3), 31.64, 25.66 (**C**H), 23.46, 22.97, 22.36 (Si**C**H_2); δ_{Si} (79.3 MHz; $CDCl_3$) -58.20 (**Si**OH), -66.98, -68.95, -69.05, -69.30 (1:2:2:2:2); *m/z* (Electrospray) 991 (60%, M), 973, 917, 862, 803, 754, 571, 516, 116 and 57.

4.2.2.8 Rearrangement of Hexaoctylsilsesquioxane with TBAF

TBAF (0.42 ml of 1 M solution in THF with 5% water) was added to OctylT_6, (0.21 g, 0.42 mmol) dissolved in deuterated chloroform (2 ml). The mixture was stirred overnight. The reaction mixture was worked up in the usual way. After extraction with water and removal of the solvent, an oily product was obtained. (0.12g mixture); ν_{max} (Nujol)/cm^{-1} 2627, 1408, 1344, 1294, 1261, 1214, 1127, 1045, 915, 886, 796 and 723; δ_H (300 MHz;

$CDCl_3$) 1.26 (96H, vbr, m, CH_2), 0.93 (24H, *t*, CH_3) and 0.62 (16H, t, $SiCH_2$); δ_C 12.08 ($SiCH_2$), 14.23 (CH_3), 22.92 (CH_2CH_2Si), 29.46(CH_2CH_3), 32.81 (CH_2), 32.09(CH_2), and δ_{Si} (79.3 MHz; $CDCl_3$) -66.63.

4.2.2.9 Rearrangement of Hexa-*p*-methoxyphenylpropylsilsesquioxane*

Hexa-*p*-methoxyphenylpropylsilsesquioxane, *p*-methylphenylpropylT_6, (0.15 g, 0.12 mmol) was dissolved in chloroform (5 ml), then TBAF (62 μl of 1 M solution in THF with 5% water) was added. The mixture was stirred at room temperature overnight, and then washed with water (3 × 10 ml). The organic layer was separated to give a white solid after removal of the solvent. A colourless crystalline product was obtained by recrystallisation from a mixed solvent of hexane and chloroform (1:1). (0.05 g, 29.2% yield); m.p.: 144°C; δ_H (300 MHz; $CDCl_3$) 0.55 (16H, t, *J* 7.71 $SiCH_2$), 1.78 (16H, quint, *J* 5.85 $SiCH_2CH_2$), 2.47 (16H, t, *J* 8.22 $SiCH_2CH_2CH_2$), 3.69 (24H, s, OCH_3), 6.71 (16H, s, *J* 6.57 CH of Ar), 6.93 (16H, s, *J* 6.21 CH of Ar); δ_C (75.5 MHz; $CDCl_3$) 12.31 ($SiCH_2$), 25.07 ($SiCH_2CH_2$), 37.97 ($SiCH_2CH_2CH_2$), 113.76 (CH of Ar), 129.36 (CH of Ar), 134.50 (CCH_2), 158.70 ($COCH_3$); δ_{Si} NMR (79.3 MHz, CDCl3, 25°C) -66.76; *m/z* (MALDI-TOF, DHB matrix) 1632 (100%, M + Na).

4.2.3 Rearrangement of hexasilsesquioxanes in the presence of spherosilicates

4.2.3.1Rearrangement of Hexasilsesquioxanes in the presence of Q_6^M/Q_8^M*

1) Rearrangement of Hexacyclohexylsilsesquioxanes in the Presence of Q_6^M*

CyT_6 (0.15 g, 0.185 mmol) and Q_6^M (0.15 g, 0.178 mmol) were dissolved in chloroform (15 ml) to which TBAF (92.5 μl of 1 M in THF with 5% water) was then added. The mixture was stirred overnight. Then washed with water (2 × 20 ml). The organic layer was separated and dried with magnesium. Removal of the solvent gave a white residue. Exaction of this residue with acetone gave a white solid product is obtained (0.1 g, 49.5%

yield); m.p.: < 400°C (dec.); ν_{max} (Nujol)/cm^{-1} 2730, 2664, 1276, 1209, 1098, 897, 867, 845 and 756; δ_H (300 MHz; $CDCl_3$) 1.71 (30H, vbr, m, CH_2), 1.20 (30H, vbr, m, CH_2), 0.75 (6H, vbr, m, CH) and 0.14 (18H, s, CH_3); δ_C (75.5 MHz; $CDCl_3$) 27.47, 26.87, 26.82, 26.61, 26.40, 26.08 (CH_2), 23.08, 22.97 (CH) and 1.35 (CH_3); δ_{Si} (79.3 MHz; $CDCl_3$) 11.45 ($SiCH_3$), -68.05 (SiCy), -68.62 (SiCy), -108.28 ($SiOSi(CH_3)_3$), (1:2:1:1); *m/z* (FAB, NOBA matrix) 1009 (15%, M - C_6H_{11}), 1089, 937, 859, 811 and 424.

2) Rearrangement of Hexacyclohexylsilsesquioxanes in the Presence of Q_8^M in the Presence of Q_8^{M*}

CyT_6 (0.5 g, 0.617 mmol) and Q_8^M (0.69 g, 0.617 mmol) were dissolved in chloroform (30 ml) to which TBAF (308 μl of 1 M solution in THF with 5% water) was added. The mixture was stirred overnight and then washed with water (3 × 30 ml). The organic layer was separated and dried with magnesium sulphate to give a white residue after removal of the solvent. Exaction of this residue with acetone gave a white solid (0.28 g, 41.8% yield); m.p <400°C (dec.); ν_{max} (Nujol)/cm^{-1} 2730, 2664, 1276, 1209, 1098, 897, 867, 845 and 756; δ_H (300 MHz; $CDCl_3$) 1.71 (30H, vbr, m, CH_2); 1.22 (30H, vbr, m, CH_2), 1.20 (6H, vbr, m, CH) and 0.75 (18H, vbr, s, $Si(CH_3)_3$); δ_C (75.5 MHz; $CDCl_3$) 27.44, 26.58 (CH_2), 23.05 (SiCH) and 1.35 ($Si(CH_3)_3$); δ_{Si} (79.3 MHz; $CDCl_3$) 11.45 ($Si(CH_3)_3$) , -68.05 (SiCy), -68.62 (SiCy), -108.28 ($SiOSi(CH_3)_3$) (1:2:1:1); *m/z* (MALDI-TOF, DHB matrix) 1201 (100%, M + Ag^+) (Found: C, 45.62; H 7.78. $C_{42}H_{84}O_{14}Si_{10}$ requires C, 46.11; H, 7.74%).

3) Rearrangement of Hexacyclopentylsilsesquioxane in the Presence of Q_8^{M*}

CpT_6 (0.5 g, 0.689 mmol) and Q_8^M (0.83 g, 0.689 mmol) were dissolved in chloroform (35 ml) to which TBAF (344 μl of 1 M solution in THF with 5% water) was added. The mixture was stirred overnight and then washed with water (2 × 30 ml). The organic layer was separated and dried with magnesium sulphate. After removal of solvent, a white

residue was obtained. Exaction of this residue with acetone gave a white solid. (0.20 g, 29.0% yield); m.p.: <400°C (dec.); ν_{max} (Nujol)/cm^{-1} 2730, 2678, 1253, 1105 (SiOSi), 949, 912, 867, 838, 759 and 712; δ_H (300 MHz; $CDCl_3$) 1.74 (12H, vbr, m, CH_2), 1.57 (36H, vbr, m, CH_2), 0.95(6H, vbr, m, CH) and 0.13 (18H, s, $Si(CH_3)_3$); δ_C (75.5 MHz; $CDCl_3$) 27.27, 27.24, 27.00, 22.14 (CH_2), 22.09, 22.04 (CH) and 1.29 (CH_3); δ_{Si} (79.3 MHz; $CDCl_3$) 11.63 ($Si(CH_3)_3$), -65.98 (SiCy), -66.50 (SiCy),, -68.62 (SiCy), -108.24, ($SiOSi(CH_3)_3$), (1:2:1:1); *m/z* (MALDI-TOF, DBH matrix) 1031 (100%, M + Na).

4) Rearrangement of Hexa-*iso*-butylsilsesquioxane with TBAF in the presence of Q_8^{M*}

Iso-butylT_6 (1.0 g, 1.53 mmol) and Q_8M_8 (1.72 g, 1.53 mmol) were dissolved in chloroform (100 ml) to which TBAF (0.77l ml of 1 M solution in THF with 5% water) was added. The mixture was stirred overnight and then washed with water (3 × 300 ml). The organic layer was separated and dried with magnesium sulphate. A white residue was obtained after removal of the solvent. Extraction of this residue with acetone gave a white solid product. (0.20 g, 28.7% yield); m.p.: <400°C (dec.); ν_{max} (Nujol)/cm^{-1} 2730, 2664, 1402, 1335, 1253, 1231, 1170, 1112, 956, 922, 867, 838, 805, 764, 741, 692 and 689; δ_H (300 MHz; $CDCl_3$) 0.03 (18H, m, $Si(CH_3)_3$), 0.52 (12H, m, CH_2Si), 0.83 (36H, m, CH_3CH), 1.73 (6H, set, *J* 6.6, CH); δ_C (75.5 MHz; $CDCl_3$) 1.24 ($Si(CH_3)_3$), 22.34 (CH_2Si), 23.76 (CH), 25.64 (CH_3); δ_{Si} (79.3 MHz; $CDCl_3$) 11.37 ($Si(CH_3)_3$), -67.03 (SiC_4H_9), -67.86 (SiC_4H_9), -108.39 ($SiOSi(CH_3)_3$), (1:2:1:1); *m/z* (MALDI-TOF, DBH matrix 1045.16 ($M + Ag^+$) (*iso*-butyl$T_6Q_2^M$).

5) Rearrangement of Hexaoctylsilsesquioxane with TBAF in the presence of Q_8^{M*}

OctylT_6 (0.3 g, 0.303 mmol) and Q_8^M (0.34 g, 0.303 mmol) were dissolved in dry chloroform (30 ml), to which TBAF (152 µl of 1 M solution in THF with 5% water) was added. The mixture was stirred at room temperature overnight and then worked up in the

usual way with water (3 × 50 ml). The organic layer with the white solid was separated and after removal of the solvent, a yellow oily residue was obtained. ν_{max} (Neat)/cm^{-1} 2968, 2923, 2864, 1469, 1409, 1372, 1335, 1261, 1075, 853, 749 and 682; δ_H (300 MHz, $CDCl_3$) 1.28 (vbr, m, CH_2), 0.89 (vbr, m, CH_3), 0.60 (vbr, m, $SiCH_2$) and 0.14 (vbr, m, $Si(CH_3)_3$); δ_C (75.5 MHz, $CDCl_3$) 32.87 (m, CH_2), 32.64 (CH_2), 31.96 (CH_2), 29.30 (CH_2), 22.67 (CH_3), 14.05 ($SiCH_2$), 11.82 (m, $SiCH_2$) and 1.22 (m, $Si(CH_3)_3$); δ_{Si} (79.3 MHz, $CDCl_3$) 11.80 ($Si(CH_3)_3$), -66.59 (SiOSi) and -67.05 (SiOSi).

6) Rearrangement of Hexa-*p*-methoxyphenylpropylsilsesquioxane with TBAF in the Presence of Q_8^{M*}

p-methoxyphenylpropylT_6 (1.0 g, 0.83 mmol) and Q_8^M (0.94 g, 0.83 mmol) were dissolved in dry chloroform (30 ml), to which TBAF (415µl of 1 M solution in THF with 5% water) was added. The mixture was stirred at room temperature overnight and then the mixture was worked up in the usual way with water (3 × 50 ml). The organic layer with the white solid was separated and after removal of solvent gave a yellow oily residue, which showed a very complex NMR.

4.2.3.2 Rearrangement of Hexasilsesquioxane with TBAF in the Presence ofQ_8^V

1) Synthesis of Q_8^V

A solution of heptane (100 ml), DMF (200 ml) and chlorodimethylvinylsilane (100 ml, 86.9 g, 731 mmol) were mixed together and stirred for 1 hour at room temperature. Then tetraethylammonium silicate (4.7 g, 2.2 mol) was slowly added to the mixture, and stirred for a further 1 hour. As it is a slightly exothermic reaction, the mixture was allowed to cool to room temperature and then further cooled to 2°C in an ice bath. Water (500 ml) was added to the mixture and the organic layer was separated from the aqueous layer and washed with water until acid free. The volatiles were removed at 25°C using a rotary

evaporator. The resulting liquid was cooled to -2°C and the product precipitated as a white solid, which could be recrystallised from acetone.[25] (1.71 g, 63.2% yield); m.p: 244-246°C; ν_{max} (Nujol)/cm^{-1} 3055, 2954, 1597, 1409, 1254, 1094, 1006, 957, 840, 788, 726, 701 and 614; δ_H (300MHz; $CDCl_3$) 0.14 (24H, s, **CH**$_3$); 5.91 (2H, m, *J* 4.2 *gem*, CH_2), 6.10 (1H, m, *J* 5.1 *cis*, *J* 14.8 *trans*, CH); δ_C (75.5 MHz; $CDCl_3$) 138.15 (**CH**), 132.69 (**CH**$_2$) and 0.43 (**CH**$_3$); δ_{Si} (79.3 MHz; $CDCl_3$) 0.55 (**Si**$(CH_3)(CHCH_2)$), -109.11 (**SiO**Si$(CH_3)(CHCH_2)$).

2) Rearrangement of Hexacyclohexylsilsesquioxane in the Presence of Q_8^V*

CyT_6 (3.87 g, 4.78 mmol) and Q_8^V (5.86 g, 4.78 mmol) were dissolved in chloroform (30 ml) to which TBAF (2.39 ml of 1 M solution in THF with 5% water) was added. The mixture was stirred overnight and then washed with water (3 × 200 ml). The organic layer was separated and dried with magnesium sulphate to give a white residue after removal of the solvent. Extraction of this residue with acetone gave a white solid. (1.79g, 33.4%yield); m.p.: < 400°C (dec.); ν_{max} (Nujol)/cm^{-1} 2723, 2664, 1276, 1253, 1194, 1105 (SiOSi), 1038, 1023, 1001, 949, 897, 838, 793 and 712; δ_H (300 MHz; $CDCl_3$) 5.96 (1H, m, *J* 5.1 *cis*, *J* 14.8 *trans*, CH), 5.73 (2H, m, *J* 8.61 *gem*, CH_2), 1.52 (30H, vbr, m, **CH**$_2$), 1.23 (30H, vbr, m, **CH**$_2$), 0.39 (6H, vbr, m, **CH**) and 0.21 (18H, s, CH_3); δ_C (75.5 MHz; $CDCl_3$) 138.50 (**CH**$_2$), 132.31 (**CH**), 27.43 (**CH**$_2$), 27.15 (**CH**$_2$), 22.31 (**CH**$_2$) and 0.05 (**CH**$_3$); δ_{Si} (79.3 MHz; $CDCl_3$) -0.53 (**Si**$(CH_3)_2(CHCH_2)$), -68.03 (**Si**Cy), -68.62 (**Si**Cy), -108.39 (**SiO**Si$(CH_3)_2(CHCH_2)$), (1:2:1:1); *m/z* (MALDI-TOF, DHB matrix) 1225 (100%, M + Ag^+)

3) Rearrangement of Hexacyclopentylsilsesquioxane in the Presence of Q_8^V*

CpT_6 (0.68 g, 0.94 mmol) and Q_8^V (1.15 g, 0.94 mmol) were dissolved in chloroform (100 ml) to which TBAF (469 μl of 1 M solution in THF with 5% water) was added. The mixture was stirred overnight and then washed with water (3 × 300 ml). The organic layer

was separated and dried with magnesium sulphate to give a white residue after removal of the solvent. Extraction of this residue with acetone gave a white solid (0.25 g, 26.0% yield); < 400 (dec.); ν_{max} (Nujol)/cm^{-1}1408, 1324, 1254, 1099, 1006, 955, 815, 839, 790, 722 and 699; δ_H (300 MHz; $CDCl_3$) 5.95 (1H, m, *J* 11.19 *cis*, *J* 14.85 *trans*, CH), 5.73 (2H, m, *J* 6.57 *gem*, CH_2), 1.59 (12H, vbr, m, CH_2), 1.41 (36H, vbr, m, CH_2), 0.84 (6H, vbr, m, CH) and 0.01 (18H, s, CH_3); δ_C (75.5 MHz; CDCl3) 138.50 (CH_2CH), 132.31 (CH_2CH), 27.43 (CH_2 of Cp), 27.15 (CH_2 of Cp), 22.31 (CH of Cp) and 0.15 (CH_3); δ_{Si} (79.3 MHz; $CDCl_3$) -0.38 ($SiCHCH_2$), -65.94 (SiCp), -66.50 (SiCp) and -108.37 ($SiOSiCHCH_2$) (1:2:1:1); *m/z* (MALDI-TOF, DHB matrix) 1141.82 (100%, M + Ag^+);

4) Derivatives of $R_6T_6Q_2R'_2$

a) Hydrosilylation of $CyT_6Q_2^v$ with tetramethyldisiloxane*

$CyT_6Q_2^v$ (0.8 g, 0.72 mmol) was dissolved in toluene (50 ml), to which tetramethyldisiloxane (3.04 g, 20 mmol) was added, followed by Karstedt catalyst (800 µl of 3% solution in toluene). The mixture was refluxed, and the reaction was followed by ^1H NMR spectroscopy, which confirmed the disappearance of the $CH=CH_2$ double bond (δ 5-6 ppm). The product was purified by chromatography using charcoal and a silica column with toluene. A waxy product was obtained after removal of the solvent (0.25 g, 27.8% yield); δ_H (300 MHz, $CDCl_3$) 1.66 (30H, vbr, m, CH_2 for C_6H_{11}), 0.15 (30H, vbr, m, CH_2 for C_6H_{11}), 0.69 (6H, vbr, m, CH for C_6H_{11}), 0.09 (4H, q, CH_2), 0.06 (4H, q, CH_2), 0.01 (6H, s, $Si(CH_3)_2$) and 0.01 (6H, s, $Si(CH_3)_2$); δ_C (75.5 MHz, $CDCl_3$) 5.08, 31.26, 27.17, 26.45, 23.40, 22.86, 22.31, 21.61, 18.48, 1.166, 1.28, and 1.18; δ_{Si} (79.3 MHz, $CDCl_3$) 12.10 ($Si(CH_3)_2$), 10.76 ($Si(CH_3)_2$), -68.07 (SiOSi), -68.60 (SiOSi) and -108.30 (SiO_4, Q); *m/z* (MALDI-TOF, DHB matrix) (100%, 1359, M + Ag^+).

b) Hydrosilylation of $CpT_6Q_2^V$ with triethoxysilane*

$CpT_6Q_2^V$ (0.2 g, 0.19 mmol) was dissolved in toluene (20 ml) to which triethoxysilane (0.08 g, 0.48 mmol) was added, followed by Karstedt catalyst (400μl of 3% solution in toluene). The mixture was refluxed and the reaction was followed by IR spectroscopy and loss of the starting material was confirmed by the disappearance of the Si-H peak at 2256 cm^{-1}). The product was purified by chromatography using a silica gel column with toluene. A waxy product was obtained after removal of the solvent. (0.23 g, 88.9% yield); δ_H (300 MHz, $CDCl_3$) 0.01 (12H, *s*, $SiCH_3$), 0.07 (4H, t, *J* 5.85 $(CH_3)_2SiCH_2$), 0.47 (4H, t, *J* 10.98, $CH_2CH_2Si(OEt)_3$), 0.87 (6H, m, vbr, CH of Cp), 1.12 (18H, m, OCH_2CH_3), 1.42 (36H, m, vbr, CH_2 of Cp), 1.64 (12H, m, vbr, CH_2 of Cp), 3.71 (12H, m, OCH_2CH_3); δ_C (75.5 MHz, $CDCl_3$) 1.32 ($Si(CH_3)_3$), 1.79 ($CH_2Si(CH_3)_3$), 2.33 ($CH_2Si(OCH_2CH_3$), 18.95 (CHSi), 22.18 (CH of Cp), 22.95 (CH of Cp), 27.81 (OCH_2CH_3), 59.12 (OCH_2CH_3); δ_{Si} (79.3 MHz, $CDCl_3$) 12.21 ($(CH_3)_2Si$), -44.51 ($SiOCH_2CH_3$), -65.91 (SiCp), -66.40 (SiCp) and –108.28 ($SiOSi(CH_3)_2$); *m/z* (MALDI-TOF, DHB matrix) (100%, 1384, $M + Na^+$), (89, 1469, $M + Ag^+$)

c) Reaction of $CyT_6Q_2^V$ with tributyltinhydride or triphenyltinhydride*

The reaction of $CyT_6Q_2^V$ with tributyltinhydride or triphenyltinhydride was carried out. However, the reactions failed, even using AIBN or H_2PtCl_6 at room temperature or reflux.

4.2.3.3 In the presence of Q_8^H, $(SiO_{3/2})_8[(OSi(CH_3)_3H]_8$

1) Synthesis of Q_8^H

A solution of heptane (100 ml), DMF (200 ml) and chlorodimethylsilane (100 ml, 86.9 g, 918 mmol) were mixed together and stirred for 1 hour at room temperature. Then tetraethylammoniun silicate (4.7 g, 2.2 mmol) was slowly added to the mixture, and the mixture was stirred for a further 1 hour. As it is a slightly exothermic reaction, the mixture

was allowed to cool to room temperature and then further cooled to 2°C in an ice bath. Water (500 ml) was added to the mixture. The organic layer was separated from the aqueous layer and washed with water until acid free. The volatiles were removed at 25°C using a rotary evaporator. The resulting liquid was cooled to -2°C and the product precipitated as a white solid, which could be recrystallised from acetone to give a colourless crystals.[15, 25] (2.0 g, 89% yield); m.p.: 265-267°C; ν_{max} (Nujol)/cm^{-1} 2961, 2143, 1422, 1260, 1099, 903, 839, 805 and 771; δ_H (300MHz, $CDCl_3$) 0.23 (48H, d, *J* 2.76 CH_3), 4.71 (8H, sept, *J* 2.7, Si**H**); δ_C (75.5 MHz, $CDCl_3$) 0.05 (**C**H_3); δ_{Si} (79.3 MHz, $CDCl_3$) 1.36 (**Si**H(CH_3)) and -108.65 (**Si**OSiH(CH_3)$_3$) (1:1).

2) Rearrangement of hexacyclohexylsilsesquioxane with TBAF in the presence of Q_8^H*

The rearrangement of hexacyclohexylsilsesquioxane with TBAF in the presence of Q_8^H was carried out as described of other spherosilicates. However, the reaction failed to give and identifiable products.

4.2.4 Treatment of hexasilsesquioxanes with TBAF in the presence of alkyltrialkoxysilanes

4.2.4.1 Rearrangement of Hexacyclohexylsilsesquioxane with TBAF in the presence of alkyltrialkoxysilanes

1) Rearrangement of Hexacyclohexylsilsesquioxane with TBAF in the presence of phenyltriethoxysilane*

CyT_6 (1.0 g, 1.23 mmol) and phenyltriethoxysilane (0.593 g, 2.46 mmol) were dissolved chloroform (50 ml) to which TBAF (0.66 ml of 1M solution in THF with 5% water) was then added. The mixture was stirred overnight and then washed with water (3 × 100 ml). The organic layer was separated and dried with magnesium sulphate to give a white residue after removal of the solvent. Exaction of this residue with acetone gave a white solid. (0.35 g, 26.6% yield); m.p: <400°C (dec.); δ_H (300 MHz; $CDCl_3$) 0.96 (6H), 1.46

(36H), 1.69 (12H), 7.34 (6H), 7.61 (4H), δ_C (75.5 MHz; $CDCl_3$) δ 22.25, 26.97, 27.33, 127.66, 130.35, 131.70, 134.08; δ_{Si} (79.3 MHz; $CDCl_3$) -68.64, -70.99.

2) Rearrangement of Hexacyclohexylsilsesquioxane with TBAF in the presence of vinyltriethoxysilane

CyT_6 (0.5 g, 0.62 mmol) and vinyltriethoxysilane (0.18 g, 1.2 mmol) were dissolved in chloroform (15 ml) to which TBAF (309 μl of 1M solution in THF with 5% water) was then added. The mixture was stirred overnight and then washed with water (3 × 50 ml). The organic layer was separated and dried with magnesium sulphate to give a white residue after removal of the solvent. Exaction of this residue with acetone gave a white solid. However, the residue gave a very complex ^{29}Si NMR.

3) Rearrangement of Hexacyclohexylsilsesquioxane with TBAF in the presence of allyltriethoxysilane*

CyclohexylT_6 (2.90g, 3.59mmol) and allyltriethoxysilane (0.73g, 3.59mmol) were dissolved in chloroform (100 ml) to which TBAF (1.79ml of 1M solution in THF with 5% water) was added. The mixture was stirred overnight and then washed with water (3 × 50 ml). The organic layer was separated and dried with magnesium sulphate to give a white residue after removal of the solvent. Exaction of this residue with acetone gave a white solid. (2.13 g, 59% yield); m.p.: <400°C (dec.); δ_H (300 MHz; $CDCl_3$) 0.96 (6H), 1.46 (36H), 1.69 (12H), 7.34 (6H), 7.61 (4H); δ_C NMR (75.5 MHz; $CDCl_3$) 22.25, 26.97, 27.33, 127.66, 130.35, 131.70, 134.08; δ_{Si} (79.3 MHz; $CDCl_3$) -65.98, -66.33, -79.37.

4) Rearrangement of Hexacyclohexylsilsesquioxane with TBAF in the presence of *p*-methoxyphenyltriethoxysilane

CyT_6 (1.0 g, 1.23 mmol) and *p*-methoxyphenypropyltriethoxysilane (0.77g, 2.46mmol) were dissolved in chloroform (80 ml) to which TBAF (0.61 ml of 1M solution in THF with

5% water) was added. The mixture was stirred overnight and then washed with water (3 × 150 ml). The organic layer was separated and dried with magnesium sulphate to give a white residue after removal of the solvent. Exaction of this residue with acetone gave a white solid. Unfortunately, the reaction did not give the expected product, but produced CyT_8, CyT_9 and *p*-methoxyphenylpropylT_8 instead.

5) Rearrangement of Hexacyclohexylsilsesquioxane with TBAF in the presence of methyltriethoxysilane

The rearrangement reaction of CyT_6 in the presence of methyltriethoxysilane was carried out as before, however, the reaction did not give any identifiable product.

4.2.4.2. Rearrangement of Hexacyclopentylsilsesquioxane with TBAF in the presence of alkyltrialkoxysilanes

1) Rearrangement of Hexacyclopentylsilsesquioxane with TBAF in the presence of phenyltriethoxysilane*

CpT_6 (1.0 g, 1.38 mmol) and phenyltriethoxysilane (0.66 g, 2.76 mmol) were dissolved in chloroform (10 ml) to which TBAF (688 μl of 1M solution in THF with 5% water) was added. The mixture was stirred overnight and then washed with water (3 × 50 ml). The organic layer was separated and dried with magnesium sulphate to give a white residue after removal of the solvent. Exaction of this residue with acetone gave a white solid. (0.2 g, 15.3%); m.p: <400°C (dcc.); δ_H (300 MHz; $CDCl_3$) 0.96 (6H), 1.46 (36H), 1.69 (12H), 7.34 (6H), 7.61 (4H); δ_C (75.5 MHz; $CDCl_3$) 22.25, 26.97, 27.33, 127.66, 130.35, 131.70, 134.08; δ_{Si} (79.3 MHz; $CDCl_3$) -65.98, -66.33, -79.37.

2) Rearrangement of Hexacyclopentylsilsesquioxane with TBAF in the presence of allyltriethoxysilane*

CpT_6 (1.03 g, 1.42 mmol) and allyltriethoxysilane (0.58 g, 2.84 mmol) were dissolved in chloroform (50 ml) to which TBAF (790 μl of 1M solution in THF with 5% water) was added. The mixture was stirred overnight and then washed with water (3 × 50 ml). The organic layer was separated and dried with magnesium sulphate to give a white residue after removal of the solvent. Exaction of this residue with acetone gave a white solid. (0.38g, 29.6% yield); m.p <400°C (dec.); δ_H (300 MHz; $CDCl_3$) 0.91 (6H, vbr, m,), 1.52 (36H, vbr, m,), 1.64 (12H, vbr, m,), 4.84 (4H, vbr, m,), 5.68 (2H, vbr, m,); δ_C (75.5 MHz; $CDCl_3$) 132.45 (CH_2=CH), 114.69 (CH_2=CH), 27.26, 26.96 (CH_2), 22.19 (SiCH), 19.62 ($SiCH_2$); δ_{Si} (79.3 MHz; $CDCl_3$) -66.48, -66.53, -71.02 (1:2:1); *m/z* (MALDI-TOF, DHB matrix), *m/z* calculated 1201 ($M + Ag^+$) found: 1201.04, 100%.

3) Rearrangement of Hexacyclopentylsilsesquioxane with TBAF in the presence of vinyltriethoxysilane

The rearrangement reaction of CpT_6 in the presence of vinyltriethoxysilane was carried out as before, however, the reaction failed to give any identifiable prodcut.

4) Rearrangement of Hexacyclopentylsilsesquioxane with TBAF in the presence of methyltriethoxysilane

CpT_6 (0.5 g, 0.68 mmol) and methyltriethoxysilane (0.25 g, 1.36 mmol) were dissolved in chloroform (10 ml) to which TBAF (344 μl of 1M solution in THF with 5% water) was then added. The mixture was stirred overnight and then washed with water (3 × 50 ml). The organic layer was separated and dried with magnesium sulphate to give a white residue after removal of the solvent. Exaction of this residue with acetone gave a white solid. However, this solid was the starting material.

4.2.4.3 Rearrangement of *p*-methoxyphenylpropylT$_6$ with TBAF in the presence of alkyltriethoxysilanes

1) Rearrangement of *p*-methoxyphenylpropylT$_6$ with TBAF in the presence of methyltriethoxysilane

p-methoxyphenypropylT$_6$ (0.5 g, 0.41 mmol) and methyltriethoxysilane (0.15 g, 0.82 mmol) were dissolved in dry chloroform (10 ml) to which TBAF (207 μl of 1 M solution in THF with 5% water) was added. The mixture was stirred at room temperature overnight and then worked up in the usual way with water (2 × 20 ml). The organic layer was separated and dried with magnesium sulphate to give a white residue after removal of the solvent. Extraction of the residue with acetone gave a white solid, however, this solid was *p*-methoxyphenypropylT$_8$. δ_H (300 MHz; $CDCl_3$) 6.96-6.72 (12H, d, Ar), 6.68-6.63 (12H, d, Ar), 3.64 (18H, s, OCH_3), 2.42 (12H, t, $ArCH_2$), 1.54 (12H, pentet, CH_2CH_2Si) and 0.50 (12H, *t*, CH_2Si); δ_C (75.5 MHz, $CDCl_3$) 157.65 (Ar), 134.40 (Ar), 129.26 (Ar), 113.65 (Ar), 55.17 (OCH_3), 37.86 ($ArCH_2$), 24.96 (CH_2CH_2Si) and 11.63 ($SiCH_2$); δ_{Si} (79.3 MHz, $CDCl_3$) -66.79.

2) Rearrangement of *p*-methoxyphenylpropylT$_6$ with TBAF in the presence of vinyltriethoxysilane

p-MethoxyphenypropylT_6 (0.5 g, 0.41 mmol) and ethyltriethoxysilane (0.12 g, 0.82 mmol) were dissolved in dry chloroform (10 ml) to which TBAF (207 μl of 1 M solution in THF with 5% water) was added. The mixture was stirred at room temperature overnight and then worked up in the usual way with water (2 × 20 ml). The organic layer was separated and dried with magnesium sulphate to give a yellow residue after removal of the solvent. However, the ^{29}Si NMR showed a very complex spectrum.

4.2.5 Rearrangement of partial cages with TBAF in the presence of Q_8^M

4.2.51 Rearrangement of $CyT_7(OH)_3$ with TBAF in the presence of Q_8^{M*}

$CyT_7(OH)_3$ (0.33 g, 0.33 mmol) and Q_8^M (0.38 g, 0.33 mmol) were dissolved in dry chloroform (20 ml) to which TBAF (169 µl of 1 M solution in THF with 5% water) was added. The mixture was stirred at room temperature overnight and then worked up in the usual way with water (3 × 50 ml). The organic layer was separated and dried with magnesium sulphate to give a white residue after removal of the solvent. Extraction of the residue with acetone gave a white solid. (0.1 g, in total). This white solid was separated by chromatography using a silica column with hexane.

The first product A was obtained (Rf = 0.79). (0.04 g, 9.8% yield); ν_{max} (Nujol)/cm^{-1} 2723, 2664, 1276, 1246, 1194, 1105, 1038, 1031, 897, 853 and 764; δ_H (300 MHz, $CDCl_3$) 1.70 (35H, vbr, m, CH_2), 1.19 (35H, vbr, m, CH_2), 0.80 (7H, vbr, m, CH) and 0.14 (9H, s, $Si(CH_3)_3$); δ_C (75.5 MHz, $CDCl_3$) 27.49 (CH_2), 26.89 (CH_2), 26.63(CH_2), 23.10 (CH) and 1.40 (CH_3); δ_{Si} (79.3 MHz, $CDCl_3$) 11.23 ($Si(CH_3)_3$), -68.09 (SiOSi), -68.64 (SiOSi), -108.24 (SiOSi, Q); *m/z* (MALDI-TOF, DHB, matrix) (100%, 1194.91, M + Ag^+).

Second fraction Rf = 0.4; (0.01g, 2.5% yield); ν_{max} (Nujol)/cm^{-1} 2723, 2671, 1253, 1201, 1083, 867, 838, 756, 697 and 667; δ_H (300 MHz, $CDCl_3$) 0.13 (*s*, $Si(CH_3)_3$), 0.73 (*m*, vbr, SiCH), 1.21 (*m*, vbr, CH_2), 1.71 (*m*, vbr, CH_2); δ_C (75.5 MHz, $CDCl_3$) 0.23 ($Si(CH_3)_3$), 22.50 (SiCH), 26.49 (CH_2) and 27.42 (CH_2); δ_{Si} (79.3 MHz, $CDCl_3$) 11.32 ($Si(CH_3)_3$), -68.05 (SiOSi), -68.52 (SiOSi), -108.30 (SiOSi, Q); *m/z* (MALDI-TOF, DHB matrix) (100%, 1201.05, M + Ag^+).

4.2.5.2 Rearrangement of $CyT_6(OH)_4$ with TBAF in the presence of Q_8^{M*}

$CyT_6(OH)_4$ (0.56 g, 0.66 mmol) and Q_8^M (0.74 g, 0.66 mmol) were dissolved in dry chloroform (20 ml) to which TBAF (330 µl of 1 M solution in THF with 5% water) was

added. The mixture was stirred at room temperature overnight and then worked up in the usual way with water (3 × 50 ml). The organic layer was separated and dried with magnesium sulphate to give a white residue after removal of the solvent. Extraction of the residue with acetone gave a white solid. (0.21 g mixture); δ_H (300 MHz, $CDCl_3$) 0.12 (*s*, vbr, $Si(CH_3)_3$), 0.85 (*m*, vbr, SiCH), 0.98 (*m*, vbr, CH_2 of Cy), 1.41 (*m*, vbr, CH_2 of Cy); δ_C (75.5 MHz, $CDCl_3$) 1.35 ($SiCH_3$), 13.66 (SiCH), 19.71 (SiCH), 22.93 ($SiCH_2$), 23.06 ($SiCH_2$), 24.08 ($SiCH_2$), 26.46 ($SiCH_2$), 26.49 ($SiCH_2$), 26.58 ($SiCH_2$), 26.79 ($SiCH_2$), 27.38 ($SiCH_2$), 27.44 ($SiCH_2$); δ_{Si} (79.3 MHz, $CDCl_3$) 11.45, -68.07, -68.64, -108.28.

4.3 Chapter Four References

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Chapter 5: Conclusions

We have investigated the synthesis of a range of silsesquioxane cages, such as the hexasilsesquioxane cage, T_6R_6, the octasilsesquioxane cage, T_8R_8 decasilsesquioxane cage, $T_{10}R_{10}$, and the dodecasilsesquioxane cage, $T_{12}R_{12}$. A number of different approaches were used to prepare the hexasilsesquioxane cages depending upon the nature of the substituent on the core. We have modified methods from the literature and obtained an efficient yield of pure hexasilsesquioxane cages. Although hydrolsilylation of T_8H_8 with a range of alkenes was employed in the initial stage of this work, we have investigated a novel method of producing a wide range of high molecular weight cages in high yield. Octasilsesquioxanes, docasilsesquioxanes and dodecasilsesquioxanes can be obtained from the reaction of alkyltrialkoxysilane with TBAF containing 5% water as a catalyst. Initial experiments suggest the water in the TBAF is involved in forming the cages. The hydrogen bonding of fluoride ion and the water produces a nucleophile, which subsequently attacks the silicon atom with loss of EtO^-. Eventually high molecular weight cages were formed. Depending upon the nature of the alkyltriethoxysilane and the solvent employed, different yields and structure of the cages were obtained. Extensive work has been carried out in our research group in order to optimise the reaction conditions and identify the intermediates.

We have investigated the rearrangement reaction of both of hexasilsesquioxane cages and octasilsesquioxane cages using a range of catalysts, including electrophiles, nucleophiles and TBAF. We have observed that the hexasilsesquioxane cage gave a higher molecular weight cage, the octasilsesquioxane in the presence of TBAF providing we leave the reaction for sufficient time. We monitored the reaction by both NMR and HPLC. A numbers of partial cages observed as intermediates, such as $R_6T_6(OH)_4$, $R_7T_7(OH)_3$ and R_9T_9OH, which have been unambiguously identified. These results suggest that the Si-O-Si linkages of the

hexasilsesquioxane cage were cleaved in the early stages to give the partial cage and were subsequently condensed to form the octasilsesquioxane cage. We also investigated the rearrangement of octasilsesquioxane cages using a range of catalysts. The higher molecular weight cages, decasilsesquioxane and dodecasilsesquioxane cages, were obtained from the rearrangement of the octasilsesquioxane cage using TBAF. We proposed that the octasilsesquioxane cage undergone a similar process to the hexasilsesquioxane cage in that the octasilsesquioxane cage is opened to give partial cages and subsequently condensed to give the closed decasilsesquioxane and dodecasilsesquioxane cages.

We also attempted the rearrangement of spherosilicate Q cages with a variety of catalysts. However, the rearrangement of these Q cages failed to give well-defined silsesquioxane cages. We developed the rearrangement reaction of hexasilsesquioxane cages, by caring out in the presence of spherosilicate cages. A novel silsesquioxane cage, $R_6T_6Q_2R'_2$, was produced. Furthermore, the rearrangement of hexasilsesquioxane cages in the presence of alkytrialkoxysilane gave another series of unique heterosubstituted silsesquioxane cages. We believe that this TBAF method is an affective route for the rearrangement reactions of silsesquioxanes. This work continues to be extensively investigated in our research group, involving the optimisation of the reaction conditions and increasing the range of functionalities attacked to the core.

Appendix of crystallographic data

This section summarises the key instrument parameters and crystal data for the single crystal X-ray structures presented in Chapter 2 and 3. The appendix is split into 6 parts, one for each structure.

Part 1:	Q_6M_6
Part 2:	CpT_6
Part 3:	*p*-methoxylphenylpropylT_6
Part 4:	CyT_9OH
Part 5:	CyT_9OTMS
Part 6:	*p*-methoxylphenylpropylT_8

The layout of each part is as follow:

Section A: Summary of crystal parameters, instrument condition and data refinement information.

Section B: Listing of atomic coordinates and thermal parameters for non-hydrogen atoms.

Section C: Structure diagrams. Hydrogens normally omitted for clarity.

Section D: Listing of key bond lengths and angles (data for C-H bonds omitted).

Part 1:

Section A: Crystal data and structure refinement.

Compound number	**2.60**
Empirical formula	$C_{18}H_{54}O_{15}Si_{12}$
Formula weight	847.69
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 10.9289(2) Å
	b = 22.2229(5) Å β = 93.5118(13)°
	c = 18.3302(4) Å
Volume	4443.53(16) Å^3
Z	4
Density (calculated)	1.267 Mg / m^3
Absorption coefficient	0.400 mm^{-1}
F(000)	1800
Crystal	Colourless block
Crystal size	0.30 × 0.20 × 0.20 mm^3
θ range for data collection	2.96 – 25.03°
Index ranges	$-13 \le h \le 12$, $-25 \le k \le 26$, $-21 \le l \le 21$
Reflections collected	30547
Independent reflections	7726 [R_{int} = 0.0429]
Completeness to θ = 25.03°	98.5 %
Absorption correction	Empirical, SORTAV
Max. and min. transmission	0.9242 and 0.8893
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7726 / 0 / 474
Goodness-of-fit on F^2	1.057
Final R indices [$F^2 > 2\sigma(F^2)$]	$R1$ = 0.0364, $wR2$ = 0.0905
R indices (all data)	$R1$ = 0.0515, $wR2$ = 0.0988
Largest diff. peak and hole	0.469 and –0.484 e Å^{-3}

Diffractometer: *Enraf Nonius KappaCCD* area detector (ϕ scans and ω scans to fill *Ewald* sphere).

Data collection and cell refinement: *Denzo* (Z. Otwinowski & W. Minor, *Methods in Enzymology* (1997) Vol. **276**: *Macromolecular Crystallography*, part A, pp. 307–326; C. W. Carter, Jr. & R. M. Sweet, Eds., Academic Press).

Absorption correction: *SORTAV* (R. H. Blessing, Acta Cryst. A**51** (1995) 33–37; R. H. Blessing, J. Appl. Cryst. **30** (1997) 421–426).

Program used to solve structure: *SHELXS97* (G. M. Sheldrick, Acta Cryst. (1990) A**46** 467–473).

Program used to refine structure: *SHELXL97* (G. M. Sheldrick (1997), University of Göttingen, Germany).

Special details:

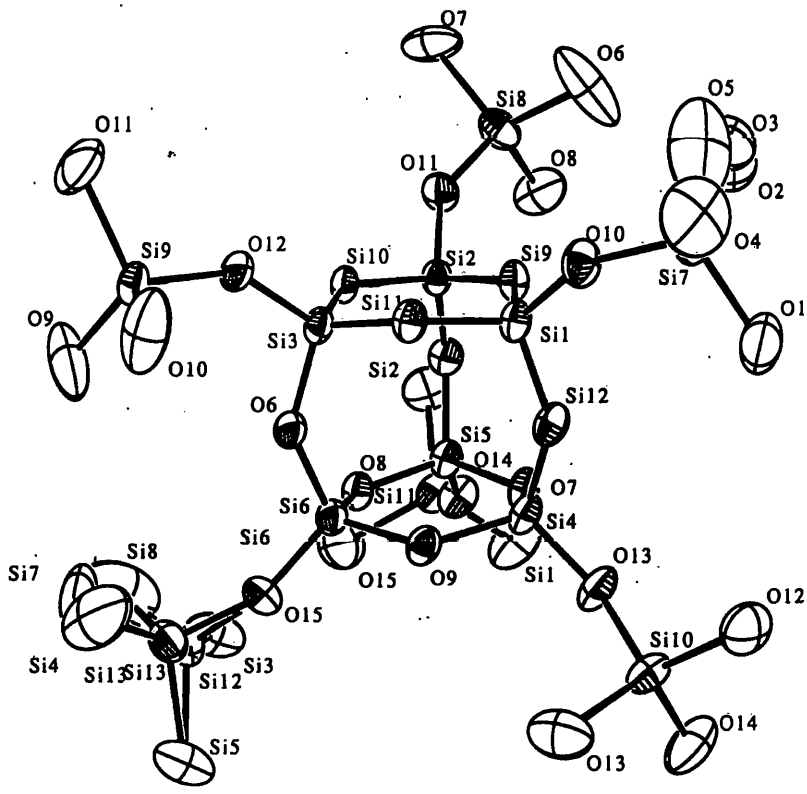
- Most methyl groups have rotational disorder and one has a positional disorder extending to the silicon atom that is split over two sites.

Section B: Atomic coordinates [$\times 10^4$], equivalent isotropic displacement parameters [$Å^2 \times 10^3$] and site occupancy factors. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	*x*	*y*	*z*	U_{eq}	*S.o.f.*
Si4	6936(1)	2397(1)	7563(1)	29(1)	1
Si6	4834(1)	2934(1)	8254(1)	28(1)	1
Si2	6008(1)	1353(1)	9365(1)	26(1)	1
Si5	7052(1)	2587(1)	9162(1)	28(1)	1
Si1	5870(1)	1156(1)	7767(1)	28(1)	1
Si3	3778(1)	1694(1)	8468(1)	26(1)	1
Si9	958(1)	1695(1)	8363(1)	31(1)	1
Si10	8166(1)	2896(1)	6176(1)	39(1)	1
Si11	8392(1)	3238(1)	10480(1)	37(1)	1
Si8	7102(1)	413(1)	10467(1)	39(1)	1
Si7	6921(1)	120(1)	6882(1)	52(1)	1
O8	5746(1)	2925(1)	8991(1)	30(1)	1
O9	5673(1)	2781(1)	7575(1)	31(1)	1
O4	6604(1)	1699(1)	7399(1)	33(1)	1
O1	6433(1)	1067(1)	8603(1)	29(1)	1
O2	4573(1)	1542(1)	9224(1)	27(1)	1
O7	7613(1)	2453(1)	8376(1)	31(1)	1

O3	4441(1)	1349(1)	7815(1)	30(1)	1
O11	6166(2)	884(1)	10017(1)	35(1)	1
O14	7967(2)	2988(1)	9658(1)	38(1)	1
O5	6808(1)	1950(1)	9558(1)	31(1)	1
O6	3815(1)	2412(1)	8320(1)	30(1)	1
O15	4186(2)	3569(1)	8147(1)	42(1)	1
O13	7811(2)	2632(1)	6973(1)	42(1)	1
O12	2401(1)	1478(1)	8515(1)	35(1)	1
O10	5980(2)	560(1)	7297(1)	39(1)	1
C5	6227(3)	83(2)	11198(2)	63(1)	1
C10	8584(3)	2259(2)	5598(2)	57(1)	1
C15	8231(3)	2624(2)	11145(2)	57(1)	1
C6	8462(3)	831(2)	10834(2)	63(1)	1
C14	10007(3)	3475(2)	10452(2)	67(1)	1
C9	−1(3)	1125(2)	8767(2)	72(1)	1
C11	6808(3)	3295(2)	5768(2)	69(1)	1
C12	9478(3)	3403(2)	6356(2)	71(1)	1
C8	617(3)	1732(2)	7375(2)	87(1)	1
C13	7422(4)	3881(2)	10695(2)	78(1)	1
C1	7999(3)	579(2)	6404(2)	86(1)	1
C7	788(3)	2431(2)	8787(3)	96(2)	1
C4	7547(5)	−163(2)	9811(2)	110(2)	1
Si12	3759(2)	4193(1)	8568(1)	36(1)	0.50
Si13	3235(2)	4091(1)	8307(1)	46(1)	0.50
C16A	4789(7)	4348(3)	9359(3)	65(2)	0.50
C17A	3762(3)	4798(1)	7889(2)	64(1)	0.50
C18A	2180(8)	4095(5)	8846(8)	124(5)	0.50
C16B	1742(7)	3851(5)	7836(6)	126(5)	0.50
C17B	3762(3)	4798(1)	7889(2)	64(1)	0.50
C18B	3061(13)	4130(6)	9274(5)	146(6)	0.50
C3A	5936(13)	−165(5)	6040(6)	99(4)	0.50
C3B	6066(11)	−502(6)	6453(7)	124(5)	0.50
C2A	7943(12)	−274(7)	7685(7)	70(3)	0.50
C2B	7463(13)	−437(7)	7429(9)	108(6)	0.50

Section C:



Section D: Selected Bond lengths [Å] and angles [°].

Si4–O13	1.5776(17)	Si1–O1	1.6274(16)
Si4–O4	1.6169(18)	Si3–O12	1.5872(15)
Si4–O9	1.6238(16)	Si3–O6	1.6201(17)
Si4–O7	1.6268(16)	Si3–O2	1.6250(15)
Si6–O15	1.5853(17)	Si3–O3	1.6284(17)
Si6–O6	1.6184(16)	Si9–O12	1.6556(16)
Si6–O9	1.6269(17)	Si9–C7	1.825(3)
Si6–O8	1.6282(16)	Si9–C8	1.829(3)
Si2–O11	1.5871(17)	Si9–C9	1.829(3)
Si2–O5	1.6154(17)	Si10–O13	1.6411(18)
Si2–O1	1.6281(16)	Si10–C12	1.838(3)
Si2–O2	1.6287(15)	Si10–C10	1.841(3)
Si5–O14	1.5848(17)	Si10–C11	1.848(3)
Si5–O5	1.6207(17)	Si11–O14	1.6464(17)
Si5–O8	1.6263(16)	Si11–C13	1.835(3)
Si5–O7	1.6266(17)	Si11–C15	1.845(3)
Si1–O10	1.5899(18)	Si11–C14	1.846(3)
Si1–O4	1.6190(17)	Si8–O11	1.6491(16)
Si1–O3	1.6271(16)	Si8–C4	1.842(4)

Si8–C6	1.844(3)	O15–Si13	1.596(2)
Si8–C5	1.846(3)	O15–Si12	1.667(3)
Si7–O10	1.6387(18)	Si12–C16A	1.813(7)
Si7–C2B	1.679(14)	Si12–C17A	1.834(4)
Si7–C3B	1.820(10)	Si12–C18A	1.842(8)
Si7–C1	1.823(4)	Si13–C18B	1.797(10)
Si7–C3A	1.933(11)	Si13–C16B	1.876(9)
Si7–C2A	1.996(13)		

O13–Si4–O4	109.20(10)	O12–Si3–O6	109.93(8)
O13–Si4–O9	112.73(9)	O12–Si3–O2	110.50(9)
O4–Si4–O9	109.02(9)	O6–Si3–O2	109.32(9)
O13–Si4–O7	110.01(9)	O12–Si3–O3	111.31(9)
O4–Si4–O7	109.13(9)	O6–Si3–O3	108.85(9)
O9–Si4–O7	106.67(8)	O2–Si3–O3	106.86(8)
O15–Si6–O6	110.06(9)	O12–Si9–C7	108.13(13)
O15–Si6–O9	111.09(9)	O12–Si9–C8	108.26(13)
O6–Si6–O9	109.24(9)	C7–Si9–C8	111.2(2)
O15–Si6–O8	111.10(9)	O12–Si9–C9	107.06(12)
O6–Si6–O8	108.60(9)	C7–Si9–C9	111.9(2)
O9–Si6–O8	106.66(8)	C8–Si9–C9	110.18(19)
O11–Si2–O5	109.94(9)	O13–Si10–C12	106.45(14)
O11–Si2–O1	111.48(9)	O13–Si10–C10	108.59(13)
O5–Si2–O1	109.26(9)	C12–Si10–C10	110.88(16)
O11–Si2–O2	110.32(9)	O13–Si10–C11	107.66(14)
O5–Si2–O2	109.10(9)	C12–Si10–C11	112.14(18)
O1–Si2–O2	106.67(8)	C10–Si10–C11	110.91(17)
O14–Si5–O5	110.40(9)	O14–Si11–C13	108.97(15)
O14–Si5–O8	111.44(9)	O14–Si11–C15	108.74(12)
O5–Si5–O8	108.90(8)	C13–Si11–C15	110.78(16)
O14–Si5–O7	110.65(9)	O14–Si11–C14	106.67(12)
O5–Si5–O7	108.60(9)	C13–Si11–C14	110.48(18)
O8–Si5–O7	106.73(8)	C15–Si11–C14	111.07(16)
O10–Si1–O4	109.85(9)	O11–Si8–C4	107.18(14)
O10–Si1–O3	110.74(9)	O11–Si8–C6	108.93(13)
O4–Si1–O3	109.14(9)	C4–Si8–C6	110.4(2)
O10–Si1–O1	111.86(9)	O11–Si8–C5	106.43(12)
O4–Si1–O1	108.29(9)	C4–Si8–C5	111.5(2)
O3–Si1–O1	106.85(8)	C6–Si8–C5	112.13(15)

O10–Si7–C2B	111.7(6)	O10–Si7–C3A	103.4(4)
O10–Si7–C3B	109.4(4)	C2B–Si7–C3A	113.2(7)
C2B–Si7–C3B	81.4(7)	C3B–Si7–C3A	32.9(5)
O10–Si7–C1	109.40(15)	C1–Si7–C3A	98.3(4)
C2B–Si7–C1	119.0(5)	O10–Si7–C2A	104.9(5)
C3B–Si7–C1	123.2(5)	C2B–Si7–C2A	22.2(7)

C3B–Si7–C2A	103.6(6)	Si6–O15–Si12	144.93(14)
C1–Si7–C2A	104.6(4)	Si13–O15–Si12	26.75(7)
C3A–Si7–C2A	134.7(6)	Si4–O13–Si10	156.22(12)
Si5–O8–Si6	130.59(10)	Si3–O12–Si9	143.02(11)
Si4–O9–Si6	129.74(10)	Si1–O10–Si7	144.99(12)
Si4–O4–Si1	138.49(11)	O15–Si12–C16A	110.5(2)
Si1–O1–Si2	130.46(10)	O15–Si12–C17A	106.50(16)
Si3–O2–Si2	130.38(10)	C16A–Si12–C17A	112.2(3)
Si5–O7–Si4	130.51(10)	O15–Si12–C18A	108.9(4)
Si1–O3–Si3	129.47(10)	C16A–Si12–C18A	110.3(6)
Si2–O11–Si8	145.99(12)	C17A–Si12–C18A	108.4(5)
Si5–O14–Si11	148.06(12)	O15–Si13–C18B	109.0(4)
Si2–O5–Si5	136.03(10)	O15–Si13–C16B	105.5(4)
Si6–O6–Si3	138.04(10)	C18B–Si13–C16B	109.0(6)
Si6–O15–Si13	156.20(14)		

Part 2:

Section A: Crystal data and structure refinement.

Compound number	**3.4**	
Empirical formula	$C_{30}H_{54}O_9Si_6$	
Formula weight	727.27	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	*Ccca*	
Unit cell dimensions	$a = 16.436(3)$ Å	$\alpha = 90°$
	$b = 22.716(5)$ Å	$\beta = 90°$
	$c = 19.437(4)$ Å	$\gamma = 90°$
Volume	7257(3) $Å^3$	
Z	8	
Density (calculated)	1.331 Mg / m^3	
Absorption coefficient	0.279 mm^{-1}	
F(000)	3120	
Crystal	Block; colourless	
Crystal size	0.2 x 0.12 x 0.12 mm^3	
θ range for data collection	3.06 – 25.03°	
Index ranges	$-19 \le h \le 19, -27 \le k \le 27, -23 \le l \le 23$	
Reflections collected	54265	
Independent reflections	3211 [$R_{int} = 0.0878$]	
Completeness to $\theta = 25.03°$	99.8 %	
Absorption correction	Semi–empirical from equivalents	
Max. and min. transmission	0.952 and 0.742	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3211 / 0 / 205	
Goodness-of-fit on F^2	1.259	
Final *R* indices [$F^2 > 2\sigma(F^2)$]	$R1 = 0.0500$, $wR2 = 0.1505$	
R indices (all data)	$R1 = 0.0671$, $wR2 = 0.1659$	

Extinction coefficient	0.0000(2)
Largest diff. peak and hole	0.546 and –0.326 e $Å^{-3}$

Diffractometer: *Enraf Nonius KappaCCD* area detector (ϕ scans and ω scans to fill *Ewald* sphere).

Data collection and cell refinement: *Denzo* (Z. Otwinowski & W. Minor, *Methods in Enzymology* (1997) Vol. **276**: *Macromolecular Crystallography*, part A, pp. 307–326; C. W. Carter, Jr. & R. M. Sweet, Eds., Academic Press).

Absorption correction: *SORTAV* (R. H. Blessing, Acta Cryst. A**51** (1995) 33–37; R. H. Blessing, J. Appl. Cryst. **30** (1997) 421–426).

Program used to solve structure: *SHELXS97* (G. M. Sheldrick, Acta Cryst. (1990) A**46** 467–473).

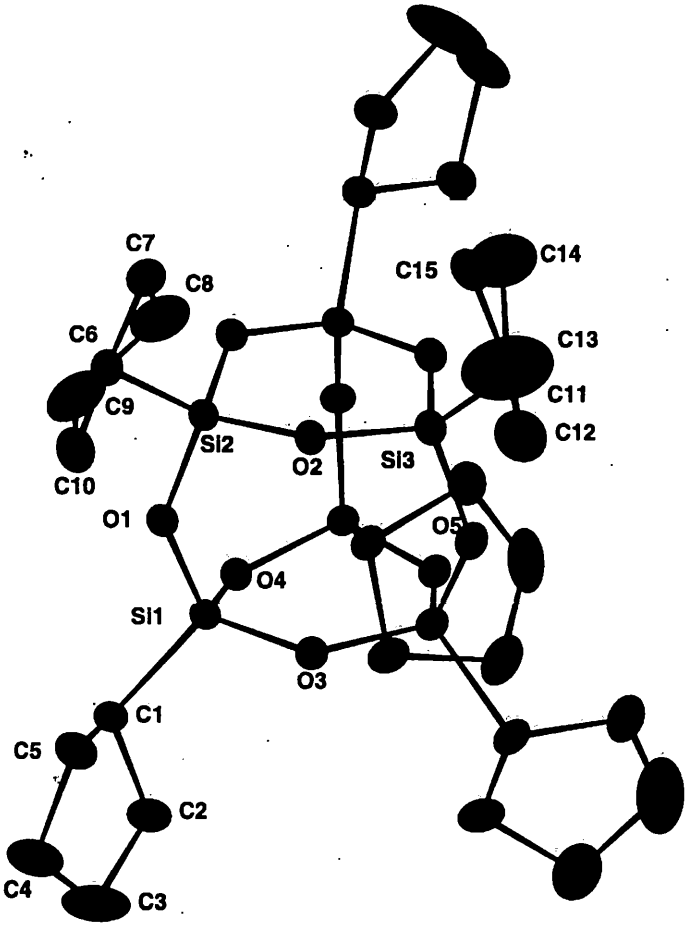
Program used to refine structure: *SHELXL97* (G. M. Sheldrick (1997), University of Göttingen, Germany).

Section B: Atomic coordinates [$\times 10^4$], equivalent isotropic displacement parameters [$Å^2 \times 10^3$] and site occupancy factors. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	*x*	*y*	*z*	U_{eq}	*S.o.f.*
Si1	1223(1)	3366(1)	2095(1)	26(1)	1
Si2	1238(1)	2124(1)	1497(1)	25(1)	1
Si3	2807(1)	3111(1)	2783(1)	29(1)	1
01	1007(1)	2817(1)	1589(1)	27(1)	1
02	2225(1)	2044(1)	1558(1)	28(1)	1
03	2213(1)	3390(1)	2193(1)	30(1)	1
04	849(1)	3248(1)	2862(1)	27(1)	1
05	3203(2)	2500	2500	32(1)	1
C1	860(2)	4055(1)	1714(1)	29(1)	1
C2	1135(2)	4618(1)	2093(2)	40(1)	1
C3	1219(4)	5092(2)	1567(2)	105(2)	1
C4	1092(3)	4810(2)	861(2)	66(1)	1
C5	1166(2)	4153(1)	976(2)	41(1)	1
C6	886(2)	1863(1)	656(1)	30(1)	1
C7	1180(2)	1231(1)	484(2)	39(1)	1
C8	1810(2)	1313(2)	–71(2)	65(1)	1
C10	1214(2)	2258(2)	59(2)	43(1)	1

C11	3603(2)	3640(1)	3020(2)	37(1)	1
C9	1513(3)	1832(2)	–484(2)	68(1)	1
C12	4222(2)	3420(2)	3550(2)	62(1)	1
C13	4334(4)	3893(3)	4048(3)	128(3)	1
C14	3887(3)	4439(2)	3828(3)	88(2)	1
C15	3250(2)	4215(2)	3339(2)	47(1)	1

Section C:



Section D: Selected Bond lengths [Å] and angles [°].

Si1–O1	1.628(2)	Si3–O5	1.6281(1
Si1–O4	1.6343(18)	Si3–O3	1.6347(1
Si1–O3	1.639(2)	Si3–O2^{i}	1.6369(1
Si1–C1	1.831(3)	Si3–C11	1.835(3)
Si2–O1	1.628(2)	O2–Si3^{i}	1.6369(1
Si2–O2	1.637(2)	O4–Si2^{i}	1.6380(1
Si2–O4^{i}	1.6380(19)	O5–Si3^{i}	1.6281(1
Si2–C6	1.831(3)		

01–Si1–04	110.10(10)	03–Si3–02^{i}	106.45(11)
01–Si1–03	108.21(10)	05–Si3–C11	110.95(14)
04–Si1–03	105.85(10)	03–Si3–C11	110.41(13)
01–Si1–C1	109.84(11)	02^{i}–Si3–C11	111.11(12)
04–Si1–C1	112.70(11)	Si1–01–Si2	139.09(13)
03–Si1–C1	109.98(12)	Si3^{i}–02–Si2	131.30(12)
01–Si2–02	109.35(10)	Si3–03–Si1	131.45(12)
01–Si2–04^{i}	108.91(10)	Si1–04–Si2^{i}	129.19(12)
02–Si2–04^{i}	105.91(10)	Si3^{i}–05–Si3	132.86(17)
01–Si2–C6	109.70(12)	C5–C1–Si1	113.3(2)
02–Si2–C6	110.02(11)	C2–C1–Si1	114.8(2)
04^{i}–Si2–C6	112.86(12)	C7–C6–Si2	113.2(2)
05–Si3–03	109.44(9)	C10–C6–Si2	111.6(2)
05–Si3–02^{i}	108.35(9)		

Symmetry transformations used to generate equivalent atoms: (i) x+0,–y+1/2,–z+1/2

Part 3:

Section A: Crystal data and structure refinement.

Compound number	**3.5e**
Empirical formula	$C_{60}H_{78}O_{15}Si_6$
Formula weight	1207.76
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*C2/c*
Unit cell dimensions	$a = 45.9349(12)$ Å
	$b = 8.0174(2)$ Å $\quad \beta = 93.9302(11)°$
	$c = 16.4720(5)$ Å
Volume	6052.0(3) Å^3
Z	4
Density (calculated)	1.326 Mg / m^3
Absorption coefficient	0.204 mm^{-1}
F(000)	2568
Crystal	Colourless block
Crystal size	$0.20 \times 0.10 \times 0.10$ mm^3
θ range for data collection	3.09 – 25.02°
Index ranges	$-54 \le h \le 53, -9 \le k \le 9, -19 \le l \le 19$
Reflections collected	8077
Independent reflections	4909 [$R_{int} = 0.0559$]
Completeness to $\theta = 25.02°$	91.7 %
Absorption correction	Empirical
Max. and min. transmission	0.9799 and 0.9603
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4909 / 0 / 368
Goodness-of-fit on F^2	0.954
Final *R* indices [$F^2 > 2\sigma(F^2)$]	$R1 = 0.0556$, $wR2 = 0.1298$
R indices (all data)	$R1 = 0.0984$, $wR2 = 0.1495$

Extinction coefficient	0.0000(2)
Largest diff. peak and hole	0.792 and –0.366 e $Å^{-3}$

Special details:

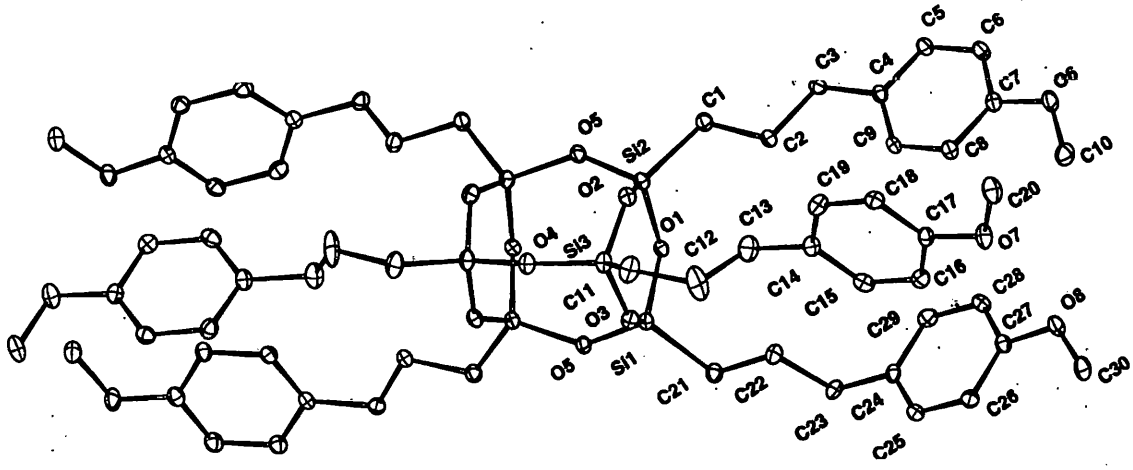
- All hydrogen atoms were placed in idealised positions and refined using a riding model.

SectionB: Atomic coordinates [$\times 10^4$], equivalent isotropic displacement parameters [$Å^2 \times 10^3$] and site occupancy factors. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	*x*	*y*	*z*	U_{eq}	*S.o.f.*	
C1	789(1)	7684(4)	3334(2)	28(1)	1	
C2	1043(1)	7492(4)	2789(2)	23(1)	1	
C3	1321(1)	8292(4)	3158(2)	25(1)	1	
C4	1595(1)	7969(4)	2724(2)	24(1)	1	
C5	1862(1)	8598(4)	3054(2)	27(1)	1	
C6	2116(1)	8286(4)	2687(2)	31(1)	1	
C7	2116(1)	7320(4)	1989(2)	28(1)	1	
C8	1854(1)	6708(4)	1647(2)	28(1)	1	
C9	1598(1)	7040(4)	2019(2)	25(1)	1	
C10	2387(1)	6110(5)	955(2)	38(1)	1	
C11	508(1)	1726(4)	1835(3)	41(1)	1	
C12	760(1)	1929(5)	1304(3)	62(2)	1	
C13	976(1)	3244(5)	1476(3)	44(1)	1	
C14	1274(1)	2949(4)	1154(2)	29(1)	1	
C15	1370(1)	3713(4)	472(2)	30(1)	1	
C16	1642(1)	3430(4)	202(2)	30(1)	1	
C17	1831(1)	2326(4)	631(2)	27(1)	1	
C18	1740(1)	1540(4)	1304(2)	28(1)	1	
C19	1466(1)	1845(4)	1565(2)	32(1)	1	
C20	2305(1)	1097(5)	773(3)	44(1)	1	
C21	264(1)	7646(4)	353(2)	28(1)	1	
C22	588(1)	7306(4)	236(2)	30(1)	1	
C23	704(1)	8316(4)	–453(2)	27(1)	1	
C24	1018(1)	7984(4)	–594(2)	25(1)	1	
C25	1097(1)	6900(4)	–1190(2)	28(1)	1	
C26	1385(1)	6573(4)	–1336(2)	27(1)	1	
C27	1605(1)	7354(4)	–856(2)	25(1)	1	
C28	1533(1)	8416(4)	–243(2)	28(1)	1	
C29	1245(1)	8740(4)	–114(2)	30(1)	1	
C30	1979(1)	6127(4)	–1610(2)	37(1)	1	
O1	322(1)	7548(2)	2087(1)	21(1)	1	
O2	471(1)	4747(3)	2792(1)	26(1)	1	

O3	205(1)	4738(3)	1334(1)	27(1)	1
O4	0	2893(4)	2500	29(1)	1
O5	−204(1)	7061(3)	1373(1)	26(1)	1
O6	2382(1)	7052(3)	1681(2)	35(1)	1
O7	2099(1)	2136(3)	319(2)	39(1)	1
O8	1897(1)	7125(3)	−940(2)	32(1)	1
Si1	142(1)	6742(1)	1292(1)	23(1)	1
Si2	441(1)	6750(1)	2958(1)	23(1)	1
Si3	296(1)	3547(1)	2115(1)	26(1)	1

Section C:



Section D: Selected Bond lengths [Å] and angles [°].

C1–C2	1.529(5)	C14–C15	1.377(5)
C1–Si2	1.831(3)	C14–C19	1.392(5)
C2–C3	1.519(4)	C15–C16	1.377(5)
C3–C4	1.511(5)	C16–C17	1.397(5)
C4–C9	1.380(5)	C17–O7	1.376(4)
C4–C5	1.399(4)	C17–C18	1.365(5)
C5–C6	1.374(5)	C18–C19	1.381(5)
C6–C7	1.387(5)	C20–O7	1.432(4)
C7–O6	1.372(4)	C21–C22	1.537(4)
C7–C8	1.385(5)	C21–Si1	1.829(4)
C8–C9	1.388(5)	C22–C23	1.521(5)
C10–O6	1.415(4)	C23–C24	1.502(4)
C11–C12	1.507(6)	C24–C25	1.377(5)
C11–Si3	1.832(4)	C24–C29	1.402(5)
C12–C13	1.464(5)	C25–C26	1.385(5)
C13–C14	1.517(5)	C26–C27	1.391(5)

C27–O8	1.371(4)	O3–Si3	1.633(2)
C27–C28	1.379(5)	O3–Si1	1.633(2)
C28–C29	1.379(5)	O4–Si3	1.6250(14)
C30–O8	1.434(4)	O4–Si3^{i}	1.6250(14)
O1–Si2	1.630(2)	O5–Si2^{i}	1.622(2)
O1–Si1	1.634(2)	O5–Si1	1.627(2)
O2–Si2	1.636(2)	Si2–O5^{i}	1.622(2)
O2–Si3	1.642(2)		

C2–C1–Si2	116.3(2)	C27–C26–C25	118.8(3)
C3–C2–C1	112.2(3)	O8–C27–C28	116.2(3)
C2–C3–C4	116.3(3)	O8–C27–C26	124.3(3)
C9–C4–C5	117.5(3)	C28–C27–C26	119.6(3)
C9–C4–C3	123.2(3)	C27–C28–C29	120.6(3)
C5–C4–C3	119.3(3)	C28–C29–C24	121.1(3)
C6–C5–C4	120.7(3)	Si2–O1–Si1	132.16(13)
C5–C6–C7	121.1(3)	Si2–O2–Si3	130.27(14)
O6–C7–C8	124.6(3)	Si3–O3–Si1	130.04(15)
O6–C7–C6	116.5(3)	Si3–O4–Si3^{i}	142.4(2)
C8–C7–C6	118.9(3)	Si2^{i}–O5–Si1	137.67(15)
C7–C8–C9	119.5(3)	C7–O6–C10	117.4(3)
C4–C9–C8	122.2(3)	C17–O7–C20	116.4(3)
C12–C11–Si3	120.2(3)	C27–O8–C30	117.4(3)
C13–C12–C11	120.3(4)	O5–Si1–O3	108.83(12)
C12–C13–C14	115.9(3)	O5–Si1–O1	108.37(12)
C15–C14–C19	116.9(3)	O3–Si1–O1	106.08(12)
C15–C14–C13	124.1(3)	O5–Si1–C21	111.40(14)
C19–C14–C13	119.0(4)	O3–Si1–C21	111.24(14)
C14–C15–C16	122.6(3)	O1–Si1–C21	110.72(14)
C15–C16–C17	119.3(4)	O5^{i}–Si2–O1	109.66(12)
O7–C17–C18	125.8(3)	O5^{i}–Si2–O2	109.37(12)
O7–C17–C16	115.0(3)	O1–Si2–O2	105.37(12)
C18–C17–C16	119.3(3)	O5^{i}–Si2–C1	108.55(15)
C17–C18–C19	120.5(3)	O1–Si2–C1	111.64(14)
C18–C19–C14	121.5(4)	O2–Si2–C1	112.21(14)
C22–C21–Si1	113.0(2)	O4–Si3–O3	108.81(11)
C23–C22–C21	113.0(3)	O4–Si3–O2	107.92(12)
C24–C23–C22	114.2(3)	O3–Si3–O2	106.20(12)
C25–C24–C29	117.0(3)	O4–Si3–C11	108.34(16)
C25–C24–C23	121.6(3)	O3–Si3–C11	112.23(17)
C29–C24–C23	121.5(3)	O2–Si3–C11	113.19(16)
C24–C25–C26	122.9(3)		

Symmetry transformations used to generate equivalent atoms: (i) –x,y,–z+1/2

Part 4:

Section A: Crystal data and structure refinement.

Compound number	**3.13**	
Empirical formula	$C_{54.50}H_{100.50}Cl_{1.50}O_{14}Si_9$	
Formula weight	1285.83	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 14.7760(5) Å	α = 90°
	b = 24.6910(5) Å	β = 92.2390(10)°
	c = 19.0762(5) Å	γ = 90°
Volume	6954.3(3) Å^3	
Z	4	
Density (calculated)	1.228 Mg / m^3	
Absorption coefficient	0.285 mm^{-1}	
F(000)	2764	
Crystal	Pyramid; colourless	
Crystal size	0.35 × 0.20 × 0.20 mm^3	
θ range for data collection	1.61 – 22.50°	
Index ranges	$-15 \le h \le 15$, $-26 \le k \le 26$, $-18 \le l \le 20$	
Reflections collected	42961	
Independent reflections	9073 [R_{int} = 0.0495]	
Completeness to θ = 22.50°	99.8 %	
Max. and min. transmission	0.9452 and 0.9069	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9073 / 586 / 702	
Goodness-of-fit on F^2	0.964	
Final R indices [$F^2 > 2\sigma(F^2)$]	$R1$ = 0.1138, $wR2$ = 0.2329	
R indices (all data)	$R1$ = 0.1434, $wR2$ = 0.2432	
Extinction coefficient	0.0025(3)	

Largest diff. peak and hole	2.020 and –0.900 e $Å^{-3}$

Diffractometer: *Enraf Nonius KappaCCD* area detector (ϕ scans and ω scans to fill *Ewald* sphere).

Data collection and cell refinement: *Denzo* (Z. Otwinowski & W. Minor, *Methods in Enzymology* (1997) Vol. **276**: *Macromolecular Crystallography*, part A, pp. 307–326; C. W. Carter, Jr. & R. M. Sweet, Eds., Academic Press).

Absorption correction: *SORTAV* (R. H. Blessing, Acta Cryst. A**51** (1995) 33–37; R. H. Blessing, J. Appl. Cryst. **30** (1997) 421–426).

Program used to solve structure: *SHELXS97* (G. M. Sheldrick, Acta Cryst. (1990) A**46** 467–473).

Program used to refine structure: *SHELXL97* (G. M. Sheldrick (1997), University of Göttingen, Germany).

Special details:

- 2 Data sets were collected, data quality not particular good
- 3 of the 9 (C_6H_{11}) units are disordered
- (C_6H_{11}) units were refined using 586 distance restraints for chemically equivalent distances
- Rest peaks were assigned to $HCCl_3$ solvent with site occupancy 0.5
- Asymmetric unit contains $(C_6H_{11})_9Si_9O_{13}OH$ 0.5 $HCCl_3$
- Highest rest peaks after final refinement are close to HCCl3 (disorder with another solvent?)
- Solvent and C-atoms involved in disorder were kept isotropic

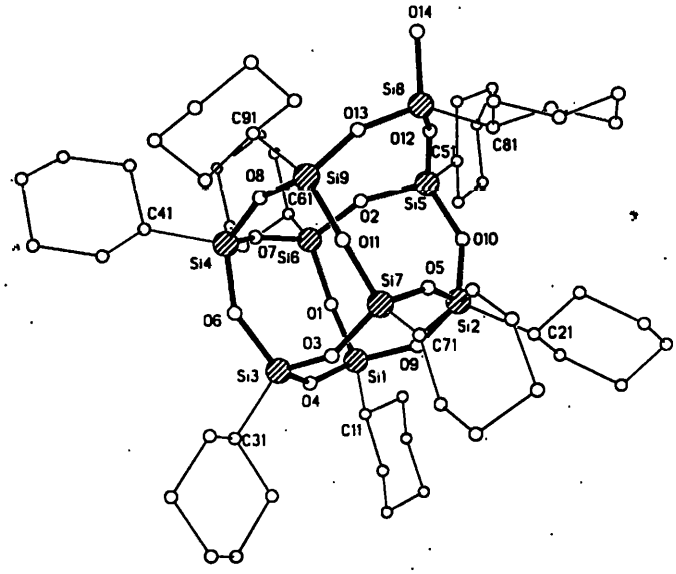
Section B: Atomic coordinates [$\times 10^4$], equivalent isotropic displacement parameters [$Å^2 \times 10^3$] and site occupancy factors. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij}

tensor.

Atom	x	y	z	U_{eq}	*S.o.f.*	
Si1	6444(2)	2505(1)	1972(1)	51(1)	1	
Si2	5928(2)	1320(1)	2366(1)	58(1)	1	
Si3	7758(2)	2556(1)	3279(1)	57(1)	1	
Si4	9317(2)	2108(1)	2381(1)	63(1)	1	
Si5	7052(2)	867(1)	1168(1)	61(1)	1	
Si6	7962(2)	2015(1)	1094(1)	55(1)	1	
Si7	7320(2)	1367(1)	3653(1)	66(1)	1	
Si8	8174(2)	64(1)	2094(2)	69(1)	1	
Si9	9131(2)	955(1)	3055(2)	74(1)	1	
O1	7108(4)	2366(2)	1337(3)	60(2)	1	
O2	7712(4)	1382(2)	1160(3)	61(2)	1	
O3	7404(5)	2019(2)	3664(3)	68(2)	1	
O4	7036(4)	2719(2)	2651(3)	58(2)	1	
O5	6671(4)	1193(2)	2985(3)	62(2)	1	
O6	8723(4)	2429(3)	2947(3)	67(2)	1	
O7	8826(4)	2140(3)	1610(3)	70(2)	1	
O8	9384(4)	1483(2)	2606(3)	69(2)	1	
O9	5913(4)	1962(2)	2192(3)	62(2)	1	
O10	6233(4)	986(2)	1683(3)	66(2)	1	
O11	8305(5)	1098(3)	3565(4)	79(2)	1	
O12	7629(5)	360(2)	1464(3)	76(2)	1	
O13	8813(5)	476(3)	2532(4)	80(2)	1	
O14	8813(5)	−398(3)	1769(4)	90(2)	1	
C11	5637(5)	3030(3)	1679(4)	52(2)	1	
C12	5043(6)	3229(4)	2257(4)	78(3)	1	
C13	4414(7)	3685(4)	1999(5)	105(4)	1	
C14	3851(6)	3518(5)	1361(6)	100(4)	1	
C15	4435(7)	3334(4)	781(5)	86(3)	1	
C16	5074(6)	2876(3)	1031(4)	74(3)	1	
C21	4797(5)	1102(3)	2631(5)	71(3)	1	
C22	4757(6)	499(3)	2777(6)	82(3)	1	
C23	3832(7)	337(5)	3050(7)	119(5)	1	
C24	3084(7)	507(5)	2547(7)	123(5)	1	
C25	3106(6)	1108(5)	2422(7)	112(5)	1	
C26	4030(6)	1274(4)	2137(5)	95(4)	1	
C31	7850(5)	3104(3)	3932(3)	54(2)	1	
C32	8382(6)	2940(3)	4595(4)	67(3)	1	
C33	8445(6)	3405(4)	5125(4)	78(3)	1	
C34	7518(6)	3607(4)	5301(4)	77(3)	1	
C35	6978(6)	3780(4)	4654(4)	73(3)	1	
C36	6928(5)	3319(3)	4109(4)	67(3)	1	
C41	10434(5)	2441(4)	2333(5)	77(3)	1	
C42	11103(6)	2137(4)	1913(5)	95(4)	1	
C43	11992(7)	2445(6)	1851(5)	114(5)	1	
C44	12378(6)	2600(5)	2564(5)	109(4)	1	
C45	11727(6)	2941(4)	2957(6)	106(4)	1	

C46	10825(6)	2637(4)	3032(4)	84(3)	1
C61	8247(5)	2185(3)	184(4)	53(2)	1
C62	8502(7)	2776(3)	96(4)	70(3)	1
C63	8705(8)	2911(3)	-666(5)	91(4)	1
C64	9421(7)	2543(3)	-943(5)	91(4)	1
C65	9177(7)	1956(3)	-867(4)	72(3)	1
C66	8971(6)	1820(3)	-101(4)	64(3)	1
C81	7313(6)	-266(3)	2671(4)	75(3)	1
C82	7752(7)	-584(4)	3274(5)	101(4)	1
C83	7048(8)	-872(4)	3703(5)	112(5)	1
C84	6454(7)	-1235(4)	3250(5)	92(4)	1
C85	5974(7)	-913(5)	2675(5)	103(4)	1
C86	6674(7)	-616(5)	2233(5)	92(4)	1
C51	6601(7)	725(4)	296(4)	83(3)	1
C52	6028(6)	1148(3)	-54(4)	70(3)	1
C53	5654(8)	1010(5)	-783(5)	108(4)	1
C54	6228(13)	634(7)	-1187(6)	96(8)	0.507(13)
C55	6551(15)	141(6)	-789(8)	93(7)	0.507(13)
C56	7088(11)	319(6)	-118(7)	79(7)	0.507(13)
C54'	5269(15)	460(6)	-891(12)	86(7)	0.493(13)
C55'	5971(14)	78(8)	-618(10)	66(6)	0.493(13)
C56'	6259(11)	177(5)	112(8)	50(5)	0.493(13)
C71	6919(9)	1143(4)	4494(6)	104(4)	1
C72	6760(8)	546(4)	4529(5)	104(4)	1
C73	6380(12)	369(5)	5228(7)	160(7)	1
C74	5570(11)	693(6)	5423(10)	103(9)	0.64(3)
C75	5840(13)	1281(6)	5489(8)	214(11)	1
C76	6157(10)	1471(5)	4760(8)	171(7)	1
C74'	6190(40)	764(11)	5805(10)	160(30)	0.36(3)
C91	10225(8)	766(4)	3522(6)	52(4)	0.643(13)
C92	10118(8)	229(4)	3895(7)	61(4)	0.643(13)
C93	10977(9)	62(4)	4310(8)	74(5)	0.643(13)
C94	11297(10)	501(5)	4804(6)	74(5)	0.643(13)
C95	11416(8)	1032(5)	4426(8)	88(6)	0.643(13)
C96	10483(7)	1183(3)	4079(5)	93(4)	1
C91'	9937(11)	715(5)	3770(9)	58(8)	0.357(13)
C92'	10601(14)	328(9)	3456(9)	63(8)	0.357(13)
C93'	11332(14)	147(7)	3995(12)	61(8)	0.357(13)
C94'	11759(12)	620(10)	4374(14)	83(10)	0.357(13)
C95'	11075(15)	989(8)	4693(9)	75(9)	0.357(13)
C100	723(15)	-29(5)	1008(6)	139(11)	0.50
C11	1167(6)	-94(3)	195(4)	145(3)	0.50
C12	749(5)	635(3)	1299(4)	115(2)	0.50
C13	1268(8)	-441(4)	1589(5)	180(4)	0.50

Section C:



Section D: Selected Bond lengths [Å] and angles [°].

Si1–O9	1.618(6)	Si8–O12	1.597(6)
Si1–O4	1.622(6)	Si8–O13	1.600(6)
Si1–O1	1.625(6)	Si8–O14	1.619(7)
Si1–C11	1.834(7)	Si8–C81	1.899(10)
Si2–O5	1.611(6)	Si9–O13	1.608(6)
Si2–O9	1.619(6)	Si9–O8	1.611(7)
Si2–O10	1.620(6)	Si9–O11	1.629(8)
Si2–C21	1.846(9)	Si9–C91'	1.871(11)
Si3–O6	1.613(7)	Si9–C91	1.874(9)
Si3–O3	1.614(7)	O9–Si1–O4	108.4(3)
Si3–O4	1.623(6)	O9–Si1–O1	109.3(3)
Si3–C31	1.841(7)	O4–Si1–O1	110.0(3)
Si4–O8	1.604(7)	O9–Si1–C11	110.4(4)
Si4–O7	1.618(6)	O4–Si1–C11	109.7(3)
Si4–O6	1.625(6)	O1–Si1–C11	109.0(3)
Si4–C41	1.850(9)	O5–Si2–O9	110.1(3)
Si5–O2	1.603(7)	O5–Si2–O10	106.7(3)
Si5–O12	1.604(6)	O9–Si2–O10	109.6(3)
Si5–O10	1.615(7)	O5–Si2–C21	109.9(4)
Si5–C51	1.802(8)	O9–Si2–C21	109.6(4)
Si6–O7	1.610(6)	O10–Si2–C21	110.8(4)
Si6–O2	1.612(6)	O6–Si3–O3	109.1(4)
Si6–O1	1.615(6)	O6–Si3–O4	108.9(3)
Si6–C61	1.850(8)	O3–Si3–O4	109.0(3)
Si7–O11	1.614(7)	O6–Si3–C31	111.3(4)
Si7–O3	1.615(6)	O3–Si3–C31	108.3(4)
Si7–O5	1.622(6)	O4–Si3–C31	110.2(3)
Si7–C71	1.818(10)	O8–Si4–O7	108.1(4)

O8–Si4–O6	108.8(4)	O1–Si6–C61	110.8(3)
O7–Si4–O6	110.2(3)	O11–Si7–O3	110.0(4)
O8–Si4–C41	113.3(4)	O11–Si7–O5	108.5(4)
O7–Si4–C41	107.6(4)	O3–Si7–O5	108.5(3)
O6–Si4–C41	108.8(4)	O11–Si7–C71	107.0(5)
O2–Si5–O12	107.9(4)	O3–Si7–C71	108.6(4)
O2–Si5–O10	109.3(3)	O5–Si7–C71	114.2(5)
O12–Si5–O10	109.2(4)	O12–Si8–O13	111.9(4)
O2–Si5–C51	110.4(4)	O12–Si8–O14	108.7(4)
O12–Si5–C51	110.3(4)	O13–Si8–O14	107.9(4)
O10–Si5–C51	109.7(4)	O12–Si8–C81	107.6(4)
O7–Si6–O2	108.5(4)	O13–Si8–C81	111.4(4)
O7–Si6–O1	109.3(3)	O14–Si8–C81	109.4(4)
O2–Si6–O1	108.3(3)	O13–Si9–O8	109.5(4)
O7–Si6–C61	109.0(4)	O13–Si9–O11	108.8(4)
O2–Si6–C61	110.8(3)		
O8–Si9–O11	109.7(4)	Si8–O13–Si9	160.9(5)
O13–Si9–C91'	112.4(5)	C16–C11–Si1	113.8(5)
O8–Si9–C91'	119.3(6)	C12–C11–Si1	113.2(5)
O11–Si9–C91'	96.0(7)	C26–C21–Si2	114.4(6)
O13–Si9–C91	109.7(4)	C22–C21–Si2	112.3(6)
O8–Si9–C91	103.9(4)	C36–C31–Si3	111.5(5)
O11–Si9–C91	115.0(5)	C32–C31–Si3	113.0(5)
C91'–Si9–C91	20.3(7)	C42–C41–Si4	114.3(6)
Si6–O1–Si1	146.0(4)	C46–C41–Si4	114.2(6)
Si5–O2–Si6	155.7(4)	C66–C61–Si6	113.0(5)
Si3–O3–Si7	147.1(4)	C62–C61–Si6	112.9(5)
Si1–O4–Si3	145.7(4)	C86–C81–Si8	110.1(6)
Si2–O5–Si7	152.8(4)	C82–C81–Si8	112.7(6)
Si3–O6–Si4	149.7(4)	C56–C51–Si5	117.0(7)
Si6–O7–Si4	149.7(5)	C56'–C51–Si5	120.5(9)
Si4–O8–Si9	155.1(5)	C52–C51–Si5	117.4(6)
Si1–O9–Si2	149.5(4)	C92–C91–Si9	109.7(7)
Si5–O10–Si2	145.1(4)	C96–C91–Si9	110.6(6)
Si7–O11–Si9	148.3(5)	C96–C91'–Si9	110.8(8)
Si8–O12–Si5	150.2(4)		

Symmetry transformations used to generate equivalent atoms:

Part 5:

Section A: Crystal data and structure refinement.

Compound number	**3.14**
Empirical formula	$C_{57}H_{99}O_{14}Si_{10}$
Formula weight 1289.26	
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell dimensions	$a = 22.731(5)$ Å
	$b = 24.504(5)$ Å
	$c = 25.241(5)$ Å
Volume	14059(5) Å^3
Z	8
Density (calculated)	1.218 Mg / m^3
Absorption coefficient	0.243 mm^{-1}
F(000)	5544
CrystalColourless block	
Crystal size	0.15 × 0.10 × 0.10 mm^3
θ range for data collection	2.93 – 23.25°
Index ranges	$-19 \le h \le 24, -26 \le k \le 27, -25 \le l \le 27$
Reflections collected	45408
Independent reflections	7641 [$R_{int} = 0.1991$]
Completeness to $\theta = 23.25°$	75.8 %
Max. and min. transmission	0.9761 and 0.9644
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7641 / 774 / 734
Goodness-of-fit on F^2	1.110
Final *R* indices [$F^2 > 2\sigma(F^2)$]	*R1* = 0.0887, *wR2* = 0.1946
R indices (all data)	*R1* = 0.2389, *wR2* = 0.2385
Extinction coefficient	0.00000(8)
Largest diff. peak and hole	0.585 and –0.267 e Å^{-3}

Special details:

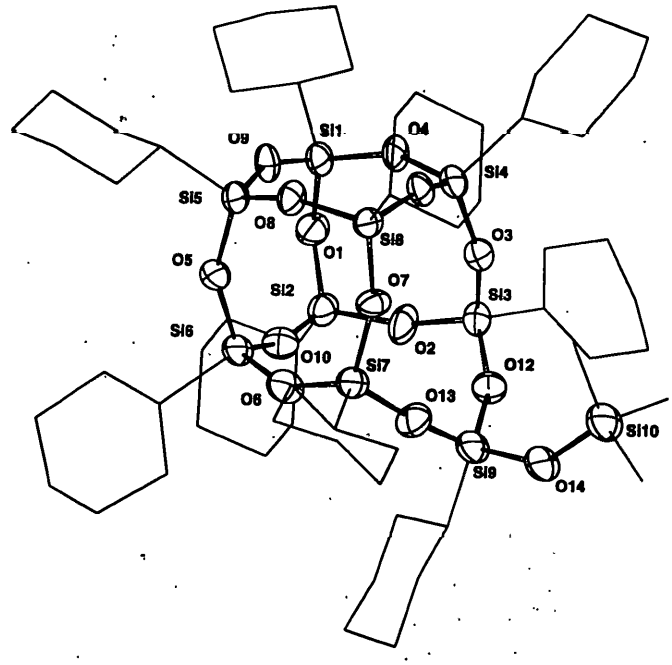
- All hydrogen atoms were placed in idealised positions and refined using a riding model. All cyclohexane rings were constrained to have the same geometry.

Section B: Atomic coordinates [$\times 10^4$], equivalent isotropic displacement parameters [$Å^2 \times 10^3$] and site occupancy factors. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	*x*	*y*	*z*	U_{eq}	*S.o.f.*	
Si1	1369(2)	2038(1)	7494(1)	61(1)	1	
Si8	15(2)	3216(1)	7994(1)	58(1)	1	
Si5	−7(2)	2040(1)	7569(1)	58(1)	1	
Si4	1386(2)	3238(1)	7901(1)	64(1)	1	
Si2	1467(2)	1646(1)	8647(1)	67(1)	1	
Si3	1829(2)	2835(1)	9007(1)	73(1)	1	
Si6	79(2)	1633(1)	8738(1)	64(1)	1	
Si7	−173(2)	2798(1)	9174(1)	65(1)	1	
Si9	926(2)	3065(1)	9913(1)	74(1)	1	
Si10	1013(2)	4300(1)	9964(2)	94(1)	1	
O8	−176(3)	2674(2)	7664(2)	59(2)	1	
O7	−46(3)	3106(2)	8617(2)	65(2)	1	
O5	−95(3)	1715(2)	8120(2)	65(2)	1	
O3	1576(3)	3176(2)	8503(3)	71(2)	1	
O6	−160(3)	2148(2)	9082(2)	76(2)	1	
O9	670(3)	1990(2)	7399(2)	59(2)	1	
O10	794(3)	1595(3)	8795(2)	68(2)	1	
O11	696(3)	3353(2)	7867(2)	60(2)	1	
O4	1532(3)	2670(2)	7590(2)	66(2)	1	
O1	1540(3)	1695(2)	8016(3)	72(2)	1	
O14	910(3)	3681(2)	10161(3)	91(3)	1	
O12	1475(3)	3012(3)	9526(3)	76(2)	1	
O13	333(3)	2962(3)	9583(3)	76(2)	1	
O2	1743(3)	2191(2)	8916(3)	86(3)	1	
C1	1764(5)	1773(4)	6907(4)	63(3)	1	
C2	2418(6)	1897(4)	6929(4)	95(4)	1	
C3	2737(5)	1684(5)	6441(5)	110(5)	1	
C4	2637(5)	1088(4)	6369(5)	93(4)	1	
C5	2001(6)	955(4)	6352(5)	95(4)	1	
C6	1688(5)	1167(4)	6849(4)	84(4)	1	
C7	−464(5)	1747(4)	7030(4)	65(3)	1	
C8	−208(5)	1211(4)	6846(4)	86(4)	1	
C9	−596(6)	947(5)	6412(5)	105(5)	1	
C10	−1202(6)	860(5)	6600(5)	106(5)	1	

C11	−1477(5)	1378(5)	6778(5)	105(5)	1
C12	−1090(5)	1648(4)	7202(4)	94(4)	1
C13	1889(5)	1045(4)	8889(4)	65(3)	1
C14	1748(5)	544(4)	8562(4)	94(4)	1
C15	2069(6)	28(4)	8767(4)	99(5)	1
C16	1866(5)	−71(4)	9309(5)	102(5)	1
C17	2015(5)	403(5)	9666(4)	96(4)	1
C18	1719(5)	923(4)	9455(4)	84(4)	1
C19	1006(5)	2591(4)	10477(4)	71(4)	1
C20	1177(6)	2036(5)	10310(5)	129(5)	1
C21	1242(6)	1621(5)	10767(5)	143(6)	1
C22	669(6)	1582(4)	11057(5)	111(5)	1
C23	500(5)	2128(5)	11264(4)	103(4)	1
C24	459(6)	2536(4)	10796(5)	111(5)	1
C25	−900(4)	2982(4)	9451(4)	62(3)	1
C26	−913(5)	3543(4)	9710(4)	72(3)	1
C27	−1527(6)	3686(5)	9921(5)	96(4)	1
C28	−1972(6)	3667(5)	9494(5)	115(5)	1
C29	−1995(5)	3128(6)	9227(6)	126(5)	1
C30	−1369(6)	2981(4)	9021(5)	97(4)	1
C31	−468(5)	3795(4)	7798(4)	68(3)	1
C32	−360(5)	4286(3)	8169(4)	78(4)	1
C33	−729(5)	4780(4)	7996(4)	95(4)	1
C34	−618(6)	4925(4)	7432(4)	110(5)	1
C35	−735(5)	4453(4)	7068(4)	99(4)	1
C36	−357(5)	3963(4)	7230(4)	78(4)	1
C37	1742(6)	3797(4)	7558(5)	108(5)	1
C38	2279(7)	3680(5)	7284(6)	178(7)	1
C39	2513(7)	4163(5)	6937(5)	180(8)	1
C40	2501(8)	4677(5)	7217(8)	234(11)	1
C41	1970(7)	4797(5)	7455(7)	166(7)	1
C42	1711(6)	4334(4)	7799(5)	129(6)	1
C43	−340(8)	1036(4)	8977(5)	154(7)	1
C44	−277(7)	549(5)	8642(5)	170(7)	1
C45	−701(8)	64(5)	8835(6)	202(9)	1
C46	−622(11)	−22(7)	9378(8)	296(14)	1
C48	−785(9)	468(7)	9662(7)	262(12)	1
C47	−314(8)	922(6)	9516(6)	210(9)	1
C49	2603(5)	2984(6)	9077(5)	121(6)	1
C50	3013(6)	2873(5)	8639(5)	114(5)	1
C51	3646(7)	3083(9)	8708(7)	222(11)	1
C52	3841(7)	3074(12)	9227(9)	301(16)	1
C53	3462(7)	3316(7)	9616(7)	187(9)	1
C54	2826(7)	3156(9)	9549(7)	223(10)	1
C55	733(6)	4374(5)	9294(4)	143(6)	1
C56	1787(6)	4456(5)	9935(6)	166(7)	1
C57	661(5)	4737(4)	10456(5)	120(5)	1

Section C:



Section D: Selected Bond lengths [Å] and angles [°].

Si1–O4	1.610(6)	Si3–O12	1.596(7)
Si1–O9	1.612(7)	Si3–O2	1.609(6)
Si1–O1	1.613(7)	Si3–O3	1.627(7)
Si1–C1	1.850(10)	Si3–C49	1.805(12)
Si8–O7	1.603(7)	Si6–O5	1.622(7)
Si8–O11	1.615(7)	Si6–O6	1.625(7)
Si8–O8	1.625(6)	Si6–O10	1.634(8)
Si8–C31	1.862(9)	Si6–C43	1.848(13)
Si5–O9	1.602(7)	Si7–O13	1.600(8)
Si5–O5	1.614(6)	Si7–O6	1.610(6)
Si5–O8	1.618(6)	Si7–O7	1.620(7)
Si5–C7	1.856(10)	Si7–C25	1.849(10)
Si4–O3	1.588(7)	Si9–O12	1.590(7)
Si4–O11	1.597(7)	Si9–O13	1.604(8)
Si4–O4	1.631(6)	Si9–O14	1.635(6)
Si4–C37	1.811(10)	Si9–C19	1.846(10)
Si2–O10	1.580(7)	Si10–O14	1.615(6)
Si2–O1	1.605(7)	Si10–C56	1.803(12)
Si2–O2	1.624(7)	Si10–C55	1.814(11)
Si2–C13	1.859(10)	Si10–C57	1.825(10)

O4–Si1–O9	108.6(3)	O4–Si1–C1	110.3(4)
O4–Si1–O1	108.8(4)	O9–Si1–C1	109.5(4)
O9–Si1–O1	108.7(4)	O1–Si1–C1	110.8(4)

O7–Si8–O11	108.2(4)	O12–Si9–O14	109.2(4)
O7–Si8–O8	110.0(3)	O13–Si9–O14	108.9(4)
O11–Si8–O8	109.0(3)	O12–Si9–C19	110.2(5)
O7–Si8–C31	109.7(4)	O13–Si9–C19	112.6(5)
O11–Si8–C31	110.7(4)	O14–Si9–C19	106.7(4)
O8–Si8–C31	109.2(4)	O14–Si10–C56	110.7(5)
O9–Si5–O5	108.1(4)	O14–Si10–C55	109.3(5)
O9–Si5–O8	110.0(3)	C56–Si10–C55	106.5(7)
O5–Si5–O8	108.4(3)	O14–Si10–C57	106.1(5)
O9–Si5–C7	108.2(4)	C56–Si10–C57	109.3(6)
O5–Si5–C7	111.8(4)	C55–Si10–C57	115.0(6)
O8–Si5–C7	110.3(4)	Si5–O8–Si8	142.8(4)
O3–Si4–O11	109.5(4)	Si8–O7–Si7	160.9(4)
O3–Si4–O4	108.9(4)	Si5–O5–Si6	149.3(4)
O11–Si4–O4	109.0(4)	Si4–O3–Si3	153.4(5)
O3–Si4–C37	114.1(5)	Si7–O6–Si6	148.4(4)
O11–Si4–C37	106.3(5)	Si5–O9–Si1	154.4(4)
O4–Si4–C37	109.0(5)	Si2–O10–Si6	159.6(5)
O10–Si2–O1	110.0(4)	Si4–O11–Si8	153.4(4)
O10–Si2–O2	109.9(4)	Si1–O4–Si4	147.8(4)
O1–Si2–O2	108.2(4)	Si2–O1–Si1	145.7(5)
O10–Si2–C13	111.1(4)	Si10–O14–Si9	138.3(5)
O1–Si2–C13	109.3(4)	Si9–O12–Si3	157.1(5)
O2–Si2–C13	108.3(4)	Si7–O13–Si9	168.5(5)
O12–Si3–O2	108.8(4)	Si3–O2–Si2	156.2(5)
O12–Si3–O3	109.0(4)	C6–C1–Si1	111.6(7)
O2–Si3–O3	110.4(4)	C2–C1–Si1	112.0(8)
O12–Si3–C49	110.9(5)	C12–C7–Si5	112.4(8)
O2–Si3–C49	109.3(6)	C8–C7–Si5	110.2(7)
O3–Si3–C49	108.5(5)	C18–C13–Si2	109.6(7)
O5–Si6–O6	109.6(4)	C14–C13–Si2	110.7(7)
O5–Si6–O10	109.5(4)	C20–C19–Si9	112.6(8)
O6–Si6–O10	109.3(4)	C24–C19–Si9	113.0(8)
O5–Si6–C43	106.7(5)	C30–C25–Si7	110.8(8)
O6–Si6–C43	105.6(6)	C26–C25–Si7	113.6(7)
O10–Si6–C43	116.0(6)	C36–C31–Si8	111.2(7)
O13–Si7–O6	109.2(4)	C32–C31–Si8	109.9(7)
O13–Si7–O7	108.3(4)	C38–C37–Si4	117.4(8)
O6–Si7–O7	109.4(3)	C42–C37–Si4	117.7(8)
O13–Si7–C25	109.7(5)	C47–C43–Si6	117.1(10)
O6–Si7–C25	108.2(4)	C44–C43–Si6	113.9(10)
O7–Si7–C25	112.0(4)	C54–C49–Si3	120.7(11)
O12–Si9–O13	109.2(4)	C50–C49–Si3	120.5(11)

Part 6:

Section A: Crystal data and structure refinement.

Compound munber	**00src434**	
Empirical formula	$C_{80}H_{104}O_{20}Si_8$	
Formula weight	1610.35	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 9.2155(2) Å	α = 81.1370(12)°
	b = 20.0378(4) Å	β = 83.6500(10)°
	c = 22.6830(5) Å	γ = 81.9340(9)°
Volume	4080.66(15) Å^3	
Z	2	
Density (calculated)	1.311 Mg / m^3	
Absorption coefficient	0.202 mm^{-1}	
F(000)	1712	
Crystal	Plate; colourless	
Crystal size	0.07 × 0.05 × 0.02 mm^3	
θ range for data collection	2.95 – 23.75°	
Index ranges	$-9 \le h \le 10$, $-20 \le k \le 22$, $-25 \le l \le 25$	
Reflections collected	25601	
Independent reflections	12287 [R_{int} = 0.0764]	
Completeness to θ = 23.75°	98.6 %	
Max. and min. transmission	0.9960 and 0.9860	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12287 / 166 / 900	
Goodness-of-fit on F^2	1.165	
Final R indices [$F^2 > 2\sigma(F^2)$]	$R1$ = 0.0978, $wR2$ = 0.1750	
R indices (all data)	$R1$ = 0.2173, $wR2$ = 0.2006	
Largest diff. peak and hole	0.899 and –0.579 e Å^{-3}	

Diffractometer: *Nonius KappaCCD* area detector (ϕ scans and ω scans to fill *Ewald* sphere).

Data collection and cell refinement: *Denzo* (Z. Otwinowski & W. Minor, *Methods in Enzymology* (1997) Vol. **276**: *Macromolecular Crystallography*, part A, pp. 307–326; C. W. Carter, Jr. & R. M. Sweet, Eds., Academic Press).

Absorption correction: *SORTAV* (R. H. Blessing, Acta Cryst. A**51** (1995) 33–37; R. H. Blessing, J. Appl. Cryst. **30** (1997) 421–426).

Program used to solve structure: *SIR97* (Cascarano et al., Acta Cryst. A52 (1996) C-79).

Program used to refine structure: *SHELXL97* (G. M. Sheldrick (1997), University of Göttingen, Germany).

Special details:

- All eight ($H_3COC_6H_4$) fragments and parts of the alkyl chains are disordered over two positions with occupancy factors for the alternative positions being close to 0.5.
- A rigid-body model and further distance restraints were applied to refine the disorder, some of the atoms involved in disorder were kept isotropic

Section B: Atomic coordinates [$\times 10^4$], equivalent isotropic displacement parameters [$Å^2 \times 10^3$] and site occupancy factors. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	*x*	*y*	*z*	U_{eq}	*S.o.f.*	
Si1	6262(2)	2338(1)	6123(1)	38(1)	1	
Si2	7637(2)	3092(1)	4925(1)	40(1)	1	
Si3	7282(2)	1868(1)	4271(1)	42(1)	1	
Si4	5918(2)	1118(1)	5466(1)	39(1)	1	
Si5	3161(2)	3035(1)	5804(1)	41(1)	1	
Si6	4541(2)	3774(1)	4625(1)	40(1)	1	
Si7	4173(2)	2540(1)	3964(1)	43(1)	1	
Si8	2800(2)	1797(1)	5146(1)	42(1)	1	
O1	7304(5)	2743(2)	5605(2)	43(1)	1	
O2	7826(5)	2514(2)	4487(2)	47(1)	1	
O3	6901(5)	1327(2)	4851(2)	45(1)	1	
O4	6197(5)	1584(2)	5954(2)	48(1)	1	
O5	4619(5)	2746(2)	6144(2)	45(1)	1	

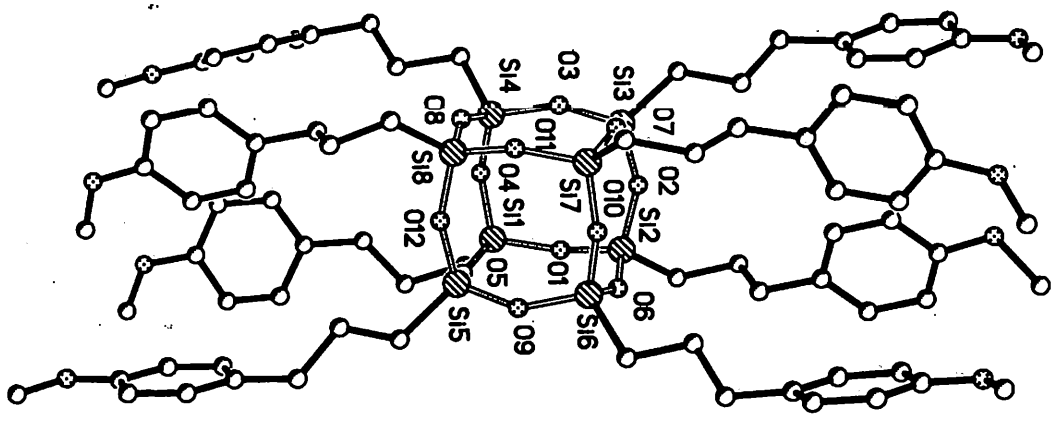
O6	6260(5)	3651(2)	4745(2)	44(1)	1
O7	5811(5)	2118(2)	3940(2)	47(1)	1
O8	4216(5)	1268(2)	5340(2)	44(1)	1
O9	3558(5)	3608(2)	5254(2)	50(1)	1
O10	4268(5)	3261(2)	4174(2)	49(1)	1
O11	3102(5)	2120(2)	4455(2)	49(1)	1
O12	2594(4)	2411(2)	5549(2)	41(1)	1
C10	6984(8)	2295(4)	6845(3)	48(2)	1
C11	5856(12)	2254(5)	7395(4)	45(4)	0.529(5)
C11'	6711(11)	1754(7)	7371(6)	56(5)	0.471(5)
C12	5136(7)	1625(4)	7525(2)	111(4)	1
C13	4466(5)	1351(3)	8134(2)	38(5)	0.529(5)
C14	4290(8)	677(3)	8297(3)	47(4)	0.529(5)
C15	3660(9)	431(3)	8867(3)	53(4)	0.529(5)
C16	3192(7)	877(4)	9273(2)	91(8)	0.529(5)
C17	3350(9)	1558(3)	9113(3)	48(4)	0.529(5)
C18	3984(8)	1790(3)	8555(3)	46(4)	0.529(5)
O01	2568(10)	698(5)	9842(3)	43(5)	0.529(5)
C19	2394(15)	1104(7)	10296(5)	62(5)	0.529(5)
C13'	4617(11)	1485(5)	8177(3)	60(7)	0.471(5)
C14'	3145(10)	1628(5)	8350(3)	49(5)	0.471(5)
C15'	2521(7)	1364(4)	8916(4)	51(5)	0.471(5)
C16'	3408(8)	956(3)	9312(3)	7(4)	0.471(5)
C17'	4893(7)	815(4)	9147(3)	40(4)	0.471(5)
C18'	5484(8)	1070(5)	8588(4)	47(4)	0.471(5)
O01'	2929(11)	668(5)	9874(3)	46(5)	0.471(5)
C19'	3810(15)	357(7)	10322(6)	51(4)	0.471(5)
C20	9358(7)	3488(4)	4848(3)	46(2)	1
C21	10028(8)	3653(4)	4198(3)	54(2)	1
C22	9118(8)	4175(4)	3827(2)	94(3)	1
C23	9674(5)	4361(3)	3183(2)	40(6)	0.545(9)
C24	10603(9)	4847(4)	3001(3)	49(4)	0.545(9)
C25	11109(9)	5014(4)	2396(3)	42(4)	0.545(9)
C26	10652(7)	4687(4)	1972(2)	33(6)	0.545(9)
C27	9706(10)	4202(5)	2148(3)	74(6)	0.545(9)
C28	9234(9)	4039(4)	2743(3)	82(6)	0.545(9)
O02	11073(10)	4803(5)	1371(2)	63(6)	0.545(9)
C29	11674(18)	5431(6)	1211(7)	80(6)	0.545(9)
C23'	9763(12)	4455(5)	3208(3)	106(13)	0.455(9)
C24'	11200(11)	4548(6)	3027(4)	44(4)	0.455(9)
C25'	11688(8)	4714(6)	2420(4)	58(6)	0.455(9)
C26'	10699(8)	4793(4)	1995(3)	48(8)	0.455(9)
C27'	9247(8)	4708(6)	2172(4)	46(5)	0.455(9)
C28'	8791(9)	4537(6)	2767(4)	48(5)	0.455(9)
O02'	11043(11)	4952(7)	1391(3)	29(5)	0.455(9)
C29'	12573(12)	4944(10)	1205(7)	57(5)	0.455(9)
C30	8726(8)	1494(4)	3751(3)	56(2)	1
C31	8997(9)	1975(4)	3149(3)	85(3)	1
C32	10151(10)	1625(5)	2742(4)	107(3)	1

C33	10445(9)	2018(4)	2114(3)	24(3)	0.500(3)
C34	11841(8)	1925(4)	1833(3)	41(4)	0.500(3)
C35	12187(6)	2233(4)	1244(3)	46(4)	0.500(3)
C36	11104(6)	2644(3)	941(2)	37(4)	0.500(3)
C37	9699(6)	2746(4)	1221(3)	46(4)	0.500(3)
C38	9374(7)	2435(4)	1795(3)	55(4)	0.500(3)
O03	11305(9)	2969(4)	367(3)	43(3)	0.500(3)
C39	10175(14)	3338(7)	43(6)	61(5)	0.500(3)
C33'	10040(11)	2169(6)	2181(4)	121(10)	0.500(3)
C34'	10489(11)	2804(5)	2069(3)	71(5)	0.500(3)
C35'	11194(9)	3048(4)	1512(3)	52(4)	0.500(3)
C36'	11430(7)	2643(3)	1064(3)	70(6)	0.500(3)
C37'	10969(10)	2006(3)	1170(4)	71(5)	0.500(3)
C38'	10297(12)	1771(5)	1720(4)	98(7)	0.500(3)
O03'	12107(10)	2823(4)	505(3)	50(3)	0.500(3)
C39'	12213(18)	2441(8)	34(6)	77(5)	0.500(3)
C40	6413(8)	223(3)	5749(3)	52(2)	1
C41	5608(10)	–4(5)	6399(4)	88(3)	1
C42	5896(11)	–700(5)	6643(4)	101(3)	1
C43	5149(9)	–905(4)	7265(3)	29(4)	0.514(3)
C44	3644(9)	–812(4)	7371(3)	43(4)	0.514(3)
C45	2934(7)	–946(4)	7949(3)	50(4)	0.514(3)
C46	3766(7)	–1171(3)	8425(2)	30(4)	0.514(3)
C47	5281(7)	–1260(4)	8326(3)	48(4)	0.514(3)
C48	5959(7)	–1134(5)	7756(3)	45(4)	0.514(3)
O04	3202(11)	–1321(5)	9008(3)	49(4)	0.514(3)
C49	1666(12)	–1203(7)	9141(6)	67(5)	0.514(3)
C43'	4962(11)	–651(5)	7247(3)	90(9)	0.486(3)
C44'	5230(11)	–323(4)	7704(4)	63(5)	0.486(3)
C45'	4911(10)	–586(4)	8308(3)	50(4)	0.486(3)
C46'	4326(8)	–1192(4)	8447(3)	49(6)	0.486(3)
C47'	4066(11)	–1531(4)	7991(4)	54(4)	0.486(3)
C48'	4368(12)	–1263(5)	7402(3)	74(6)	0.486(3)
O04'	3965(13)	–1498(5)	9017(3)	59(4)	0.486(3)
C49'	3434(17)	–2132(6)	9160(7)	64(5)	0.486(3)
C50	1730(7)	3422(3)	6318(3)	45(2)	1
C51	1235(7)	2984(3)	6893(3)	44(2)	1
C52	130(7)	3384(3)	7275(2)	48(2)	1
C53	–578(5)	3086(2)	7868(2)	36(5)	0.514(3)
C54	–2075(5)	3154(3)	8006(2)	43(4)	0.514(3)
C55	–2715(5)	2873(4)	8564(3)	47(4)	0.514(3)
C56	–1820(7)	2524(3)	8986(2)	47(4)	0.514(3)
C57	–313(6)	2458(4)	8855(2)	48(4)	0.514(3)
C58	296(5)	2730(3)	8305(2)	47(4)	0.514(3)
O05	–2313(9)	2226(4)	9543(2)	47(3)	0.514(3)
C59	–3844(11)	2313(7)	9679(7)	60(4)	0.514(3)
C53'	–268(10)	2930(4)	7910(3)	37(5)	0.486(3)

C54'	−466(11)	3220(3)	8428(4)	41(4)	0.486(3)
C55'	−1029(10)	2876(3)	8973(3)	52(5)	0.486(3)
C56'	−1380(8)	2227(3)	8992(3)	48(5)	0.486(3)
C57'	−1171(9)	1927(3)	8476(3)	44(4)	0.486(3)
C58'	−635(10)	2274(4)	7944(3)	37(4)	0.486(3)
O05'	−1940(12)	1842(4)	9496(3)	75(5)	0.486(3)
C59'	−2480(5)	1218(2)	9527(2)	48(4)	0.486(3)
C60	4040(5)	4673(2)	4284(2)	43(2)	1
C61	4827(5)	4829(2)	3661(2)	46(2)	1
C62	4359(7)	5570(3)	3382(2)	52(2)	1
C63	4962(5)	5824(2)	2757(2)	19(3)	0.500(3)
C64	6443(5)	5775(3)	2582(2)	46(4)	0.500(3)
C65	6984(5)	6016(4)	1996(2)	34(4)	0.500(3)
C66	6008(6)	6315(3)	1586(2)	47(4)	0.500(3)
C67	4517(6)	6374(3)	1759(2)	40(4)	0.500(3)
C68	4004(5)	6128(3)	2332(2)	45(4)	0.500(3)
O06	6401(8)	6566(4)	1003(2)	48(3)	0.500(3)
C69	5398(14)	6854(7)	587(5)	59(5)	0.500(3)
C63'	5069(8)	5608(5)	2719(3)	55(5)	0.500(3)
C64'	5742(9)	6189(4)	2584(3)	36(3)	0.500(3)
C65'	6386(9)	6394(3)	2006(3)	48(5)	0.500(3)
C66'	6330(6)	6007(3)	1559(2)	60(5)	0.500(3)
C67'	5643(8)	5426(3)	1688(3)	44(4)	0.500(3)
C68'	5033(9)	5227(4)	2258(3)	49(4)	0.500(3)
O06'	6921(10)	6153(5)	980(3)	52(3)	0.500(3)
C69'	6875(17)	5747(7)	530(6)	65(5)	0.500(3)
C70	3462(9)	2679(4)	3231(3)	58(2)	1
C71	4498(12)	3073(4)	2769(3)	98(4)	1
C72	4979(14)	3020(7)	2308(5)	220(17)	0.500(3)
C73	5540(10)	3444(5)	1745(4)	73(6)	0.500(3)
C74	5503(11)	3271(4)	1185(5)	83(6)	0.500(3)
C75	6034(10)	3673(4)	665(4)	64(5)	0.500(3)
C76	6620(6)	4254(3)	716(3)	52(4)	0.500(3)
C77	6678(9)	4430(4)	1277(3)	51(4)	0.500(3)
C78	6138(11)	4035(5)	1782(3)	72(5)	0.500(3)
O07	7166(10)	4688(5)	244(3)	63(3)	0.500(3)
C79	7954(16)	5221(6)	295(7)	59(5)	0.500(3)
C72'	3918(9)	3332(4)	2198(3)	42(4)	0.500(3)
C73'	4881(7)	3568(3)	1648(3)	35(4)	0.500(3)
C74'	4325(6)	3855(4)	1117(3)	40(4)	0.500(3)
C75'	5243(6)	4071(4)	607(3)	48(4)	0.500(3)
C76'	6742(6)	3988(3)	637(3)	52(5)	0.500(3)
C77'	7315(6)	3693(4)	1167(3)	50(4)	0.500(3)
C78'	6401(7)	3492(4)	1664(3)	41(4)	0.500(3)
O07'	7746(8)	4180(5)	173(3)	58(3)	0.500(3)
C79'	9279(11)	4063(7)	151(7)	57(4)	0.500(3)
C80	1131(8)	1378(4)	5257(3)	52(2)	1
C81	387(10)	1315(6)	5895(3)	21(3)	0.514(3)

C82	1384(10)	889(5)	6338(3)	70(6)	0.514(3)
C83	711(7)	698(3)	6966(2)	24(6)	0.514(3)
C84	−227(9)	210(4)	7110(3)	39(4)	0.514(3)
C85	−845(9)	40(4)	7699(3)	35(4)	0.514(3)
C86	−515(7)	374(3)	8144(2)	47(4)	0.514(3)
C87	414(9)	870(4)	8004(3)	52(4)	0.514(3)
C88	1024(8)	1026(4)	7426(3)	49(4)	0.514(3)
O08	−1044(9)	252(4)	8734(3)	51(3)	0.514(3)
C89	−795(17)	607(7)	9191(5)	58(4)	0.514(3)
C81'	720(30)	854(10)	5781(5)	140(10)	0.486(3)
C82'	1052(17)	983(7)	6328(4)	210(20)	0.486(3)
C83'	565(12)	672(5)	6952(3)	108(15)	0.486(3)
C84'	−825(11)	496(6)	7113(4)	48(5)	0.486(3)
C85'	−1259(8)	207(5)	7699(4)	48(6)	0.486(3)
C86'	−271(8)	103(4)	8126(3)	58(5)	0.486(3)
C87'	1126(8)	285(5)	7972(4)	50(4)	0.486(3)
C88'	1539(10)	560(5)	7395(4)	71(5)	0.486(3)
O08'	−562(11)	−175(6)	8711(3)	69(4)	0.486(3)
C89'	487(16)	−345(8)	9129(7)	72(5)	0.486(3)

Section C:



Section D: Bond lengths [Å] and angles [°]

Si1–O5	1.616(5)	Si3–O7	1.604(5)
Si1–O1	1.623(5)	Si3–O3	1.611(5)
Si1–O4	1.625(5)	Si3–O2	1.611(5)
Si1–C10	1.822(6)	Si3–C30	1.836(7)
Si2–O1	1.608(4)	Si4–O8	1.604(5)
Si2–O6	1.614(5)	Si4–O3	1.608(5)
Si2–O2	1.618(4)	Si4–O4	1.615(4)
Si2–C20	1.851(6)	Si4–C40	1.821(7)

Si5–O9	1.607(5)
Si5–O5	1.615(5)
Si5–O12	1.626(4)
Si5–C50	1.830(6)
Si6–O6	1.616(5)
Si6–O10	1.618(5)
Si6–O9	1.619(5)
Si6–C60	1.864(5)
Si7–O10	1.606(5)
Si7–O11	1.619(5)
Si7–O7	1.623(5)
Si7–C70	1.821(7)
Si8–O11	1.611(5)
Si8–O8	1.618(5)
Si8–O12	1.622(4)
Si8–C80	1.829(7)

O5–Si1–O1	108.8(2)
O5–Si1–O4	108.8(2)
O1–Si1–O4	108.9(2)
O5–Si1–C10	109.2(3)
O1–Si1–C10	109.4(3)
O4–Si1–C10	111.7(3)
O1–Si2–O6	108.9(2)
O1–Si2–O2	109.1(2)
O6–Si2–O2	108.9(2)
O1–Si2–C20	110.0(3)
O6–Si2–C20	111.0(3)
O2–Si2–C20	109.0(3)
O7–Si3–O3	108.4(2)
O7–Si3–O2	108.9(3)
O3–Si3–O2	108.9(2)
O7–Si3–C30	109.7(3)
O3–Si3–C30	111.5(3)
O2–Si3–C30	109.3(3)
O8–Si4–O3	108.5(2)
O8–Si4–O4	108.5(2)
O3–Si4–O4	109.0(3)
O8–Si4–C40	110.9(3)
O3–Si4–C40	110.2(3)
O4–Si4–C40	109.6(3)
O9–Si5–O5	109.2(3)
O9–Si5–O12	109.3(2)
O5–Si5–O12	108.7(2)
O9–Si5–C50	108.5(3)
O5–Si5–C50	110.3(3)
O12–Si5–C50	110.8(3)
O6–Si6–O10	108.6(2)
O6–Si6–O9	108.9(2)
O10–Si6–O9	109.1(3)
O6–Si6–C60	109.7(2)
O10–Si6–C60	110.0(2)
O9–Si6–C60	110.4(2)
O10–Si7–O11	108.8(2)
O10–Si7–O7	108.2(3)
O11–Si7–O7	108.8(3)
O10–Si7–C70	109.5(3)
O11–Si7–C70	110.5(3)
O7–Si7–C70	110.9(3)
O11–Si8–O8	109.0(3)
O11–Si8–O12	108.0(3)
O8–Si8–O12	108.7(2)
O11–Si8–C80	110.6(3)
O8–Si8–C80	111.2(3)
O12–Si8–C80	109.4(3)
Si2–O1–Si1	150.8(3)
Si3–O2–Si2	150.9(3)
Si4–O3–Si3	150.7(3)
Si4–O4–Si1	148.6(3)
Si5–O5–Si1	148.5(3)
Si2–O6–Si6	145.7(3)
Si3–O7–Si7	147.1(3)
Si4–O8–Si8	150.3(3)
Si5–O9–Si6	146.1(3)
Si7–O10–Si6	156.6(3)
Si8–O11–Si7	146.2(3)
Si8–O12–Si5	153.2(3)
C11'–C10–Si1	123.9(7)
C11–C10–Si1	116.2(6)
Si1–C10–H10A	108.2
Si1–C10–H10B	108.2
C21–C20–Si2	114.6(5)
Si2–C20–H20A	108.6
Si2–C20–H20B	108.6
C31–C30–Si3	113.1(5)
Si3–C30–H30A	109.0
Si3–C30–H30B	109.0
C41–C40–Si4	113.2(5)
Si4–C40–H40A	108.9
Si4–C40–H40B	108.9
C51–C50–Si5	117.9(5)
Si5–C50–H50A	107.8

Si5–C50–H50B	107.8	Si7–C70–H70B	109.7
C61–C60–Si6	112.00(16)	C81–C80–Si8	114.9(6)
Si6–C60–H60A	109.2	Si8–C80–H80A	108.5
Si6–C60–H60B	109.2	Si8–C80–H80B	108.5
C71–C70–Si7	109.9(5)		
Si7–C70–H70A	109.7		